AL.2.1991-60

A Review of the Modified Wood Pulping & Bleaching Processes Proposed for **Alberta • Pacific** Forest Industries Inc. Pulp Mill

CANADIANA

JAN 22 1991

By the **Alberta • Pacific** Scientific Review Panel

October, 1990

Printed on Recycled Paper

THE ALBERTA - PACIFIC SCIENTIFIC REVIEW PANEL

A Review of the Modified Wood Pulping & Bleaching Processes
Proposed for
Alberta-Pacific Forest Industries Inc. Pulp Mill

ERRATA

CANADIANA

JAN 22 1991

Page 13, Table 3.3.1, line 10; "913 cu" should read "913 $cu_{(a)}$".

Page 27, line 29; "it would designed" should read "it would be designed".

Page 35, Figure 5.3.1, "Reeve (1990)" should read "Reeve (1990b)".

Page 37, line 24; "Berry et al (1988)" should read "Berry et al (1989)".

Page 38, Tables 5.3.1 and 5.3.2, Note (a) should read "From Rappe et al 1989".

Page 46, line 23; "Dr. J. Eisenreich" should read "Dr. S.J. Eisenreich".

Page 48, Insert; Berry, R.M., Fleming, B.I., Voss, R.H., Luthe, C.E. and Wrist, P.E. (1989). "Toward preventing the formation of dioxins during chemical pulp bleaching". Pulp & Paper Canada 90(8):48-58.

Page 49, line 20; "knbica" should read "Kubica".

Page 49, line 22; "Malter-Muller C., "should read "Matter-Muller C.,".

Page 49, at line 31, the reference to PAPRICAN (1990) on page 29 should be inserted.

Page 49, line 36; "Univeristy" should read "University".

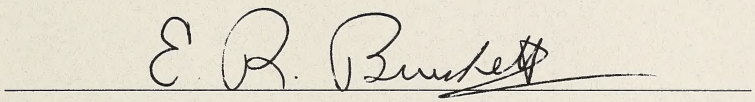
Page 52, last reference should read "Torregrossa, L., D. Justice, R. Schleinkofer, K. Vogel, and O. Luthi (1976). "Decomposition of Gaseous Chlorine Dioxide". Tappi Journal, 59(11):92-93.

Page 53, line 10; "continous" should read "continuous".

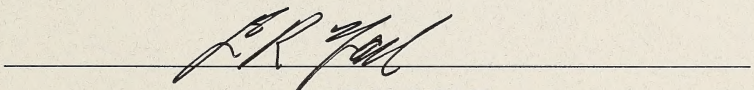
Page 55, line 4 and line 8; "CPs < 12.5 g" should read "CPs < 12.5 kg".

The Alberta-Pacific Scientific Review Panel

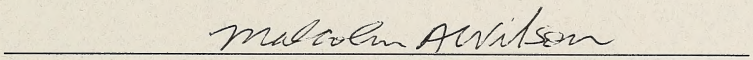
This report is respectfully submitted to the Alberta Minister of the Environment.



Edward R. Brushett, Chairman



Eric R. Hall, Ph.D.



Malcolm A. Wilson, Ph.D.

Dated at the City of Edmonton, in the Province of Alberta, this 1st day of October, 1990.

Digitized by the Internet Archive
in 2016

https://archive.org/details/reviewofmodified00albe_0

A Review of the Modified Wood Pulping & Bleaching Processes Proposed for **Alberta • Pacific** Forest Industries Inc. Pulp Mill

By the **Alberta • Pacific**
Scientific Review Panel

October, 1990

Additional copies of this report and the list of submissions to the Panel are available from:

Alberta Environment
Publications Centre, 14th Floor
Oxbridge Place
9820 106 Street
Edmoton, Alberta
T5K 2J6

(403) 422-2813

Acknowledgements

This report could not have been completed without the valued assistance and advice of the Panel's office staff, Ms. Kathryn Hart, Dr. George Kupfer and Ms. Mary Ann Robinson. Their patience and support is greatly appreciated. The Panel gives additional thanks to legal counsel, Mr. Richard Neufeld and its technical advisors Dr. Douglas Reeve and Dr. Harald Thimm. Also appreciation is extended to Mr. Garry Moore and staff and Mrs. Nancy Van Mechelen, who assisted in the Athabasca Workshop sessions.

The Review Panel thanks all the submittors and presentors who filed written and/or oral information. Also, appreciation is extended to Alberta Environment and its staff who facilitated the Panel's work. Alberta-Pacific and its staff and consultants also contributed to our process throughout the Review.

Executive Summary

Alberta-Pacific Forest Industries Inc. ("Alberta-Pacific") proposes to build and operate a bleached kraft pulp mill near the Town of Athabasca. Effluent from the mill would, following secondary treatment, be discharged into the Athabasca River.

An Environmental Impact Assessment review process undertaken by a joint provincial-federal board recommended that the project not proceed, primarily because of concern about the discharge of chlorinated organic compounds to the Athabasca River.

Subsequently, Alberta-Pacific released details of revisions to the pulping and bleaching processes at the proposed mill. According to Alberta-Pacific, these revisions would reduce the rate of discharge of chlorinated organic compounds. Whereas the original proposal implied AOX (Adsorbable Organic Halogen) discharges of up to 1.3 kilograms per air dried tonne (kg/ADt) of pulp, Alberta-Pacific asserted that its revised proposal would result in rates approximating 0.25 kg/ADt.

The Alberta-Pacific Scientific Review Panel was created by Ministerial Order 9/90 and was directed to assess the technical feasibility of the proposed design. This direction required the Panel to determine whether it is possible to design, construct and operate a pulp mill in the manner proposed, and to assess whether the resultant effluent would have the characteristics predicted by Alberta-Pacific.

The Panel conducted a two month long assessment of the revised proposal. During this period the Panel collected information and data from independent sources and commissioned submissions from technical experts on several aspects of the proposed technology. The Panel also engaged the services of two technical advisors to assist with the collection and interpretation of information. The Panel and its advisors also made one site visit to a pulp mill which utilizes similar technology to that proposed by Alberta-Pacific. These investigative activities culminated in a three day public Workshop in the Town of Athabasca from September 12 to 14, 1990.

Following the Athabasca Workshop, the Panel reviewed the information it had collected. This review extended to the level of an examination of chemical analytical results and the related analytical protocols. Due to the minimal numbers of substantiating data presented by Alberta-Pacific, the Panel compiled and analyzed data from other sources for comparison to the Alberta-Pacific information.

As a result of this investigation, the Panel concluded that it is technically feasible to design, construct and operate a bleached kraft pulp mill utilizing the technology proposed by Alberta-Pacific. Each of the revised processes now proposed have been proven by previous operation in industrial settings. Although they have not been utilized together in a single fibreline, the Panel was satisfied that it is feasible to do so. The Panel also concluded that the revised fibreline incorporates a sufficient degree of robustness to consistently achieve the chlorinated organic matter discharge rates forecasted by the Panel. Additional mitigating options are available to allow retrofitting of the Alberta-Pacific mill to further reduce the organochlorine discharge, if required. The Panel did not feel that a continuous flow pilot study was necessary to demonstrate the operational feasibility of the revised fibreline.

The Panel reviewed the design of the proposed wastewater treatment facility. Although the design of the facility is still evolving, the Panel is satisfied that the basic approach taken appears to be adequate. The Panel determined that the proposed fibreline and wastewater treatment technology is capable of limiting waterborne discharges of AOX to 0.32 kg/ADt for hardwood pulp, and 0.49 kg/ADt for softwood pulps, over the long term. The long term hardwood plus softwood weighted average would be less than 0.35 kg/ADt. These estimates are significantly different from those projected by Alberta-Pacific, and they have been calculated at a defined level of confidence. The Panel also concluded that waterborne discharges of chlorophenolic compounds would not exceed 4.0 g/ADt. The long term hardwood plus softwood weighted average discharge would be less than 840 mg/ADt. It was also determined that the bleach plant technology would not produce detectable increases of 2,3,7,8-tetrachlorodibenzo-para-dioxin or 2,3,7,8-tetrachlorodibenzofuran above background levels.

It was concluded that airborne emissions of volatile organic matter during secondary treatment would be less than 12% of the AOX produced in the bleach plant. Further, the incineration of sludges would not result in significant emissions of AOX or chlorinated compounds to the environment.

After reviewing the issue of accidental discharges, the Panel concluded that the mill can be designed with adequate safety features to prevent accidental releases of chlorinated organic matter.

The Panel's Terms of Reference precluded it from considering environmental impacts of the revised pulp mill. Therefore, the Panel did not make any assessment of the portions of the proposal that dealt with the toxicity of AOX, nor did it assess claims made by Alberta-Pacific to be able to achieve "environmental harmony" with the modified proposal. Nevertheless, a significant number of the written submissions and Workshop presentations focussed on this issue.

Table of Contents

Page

Acknowledgements

Executive Summary

List of Abbreviations

Section 1—Introduction 1

1.1 Historical Context 1
1.2 Terms of Reference 4
1.3 Investigations and Advisors 5
1.4 Submissions Received 6
1.5 Submissions Presented for Augmentation/Clarification 6
1.6 The Athabasca Workshop 7
1.7 References 7

Section 2—Preface to the Scientific Review 8

2.1 The Scope of the Panel's Review 8
2.2 Science Versus Industrial Design 8

Section 3—The Revised Pulp Mill Proposal 10

3.1 Description 10
3.2 Quantitative Changes 12
3.3 Revised Fibreline Treated Effluent Characteristics 13
3.4 The Toxicity of Chlorinated Organic Compounds in Revised Fibreline Treated Effluent 14
3.5 References 14

Section 4—Technical Feasibility of Revised Pulping and Bleaching Processes 16

4.1 Extended Modified Continuous Cooking (EMCC) 16
4.1.1 Extent of Delignification 18
4.1.2 Pulp Strength 18
4.1.3 Pulp Yield 19
4.1.4 Digester Runnability 19
4.1.5 Effects on Downstream Pulp Processing 20
4.1.6 Extent of Operating Experience 21

Page

4.2 Oxygen Delignification 22
4.3 Pulp Bleaching 22
4.3.1 100% Chlorine Dioxide Substitution 22
4.3.2 Peroxide Addition to the Pressurized E_o Stage 23
4.4.3 Overall Bleach Plant Performance and Chemical Requirements 23
4.4 Feasibility of the Combined Unit Processes 25
4.5 Robustness of the Proposed Design 26
4.6 References 28

Section 5—Expected Effluent Characteristics 30

5.1 The Nature and Abundance of Chlorinated Organic Compounds in Pulp Bleaching Effluents 30
5.2 The Mechanism of Formation of Chlorinated Organic Compounds in Pulp Mill Effluents 32
5.3 The Quantities of AOX Produced in the Revised Fibreline Mill 34
5.4 The Analysis of Chlorinated Organic Compounds in Pulping Effluents 39
5.5 Effluent Treatment 40
5.5.1 Introduction 40
5.5.2 Wastewater Treatment Plant Description 40
5.5.3 Evaluation of Wastewater Plant Design 40
5.5.4 Effluent Treatment Plant Performance 42
5.5.5 Dioxin and Furan Removal Efficiency 45
5.5.6 Sludge Disposal 45
5.5.7 Volatilization of AOX 46
5.5.8 Chlorate in Treated Effluents 47
5.6 References 47

Section 6—Accidental Discharges 51

6.1 References 52

Section 7—Conclusions 53

7.1 Technical Feasibility of Revised Pulping and Bleaching Processes 53
7.2 Expected Effluent Characteristics 53

Appendix 1—Ministerial Order No. 9/90

Appendix 2—Workshop Program

Appendix 3—Submission List

Appendix 4—The Panel Members' Biographies

List of Abbreviations

ADt	air dry metric tonnes
AOX	adsorbable organic halogen
BOD_5	5-day biochemical oxygen demand
CPPA	Canadian Pulp and Paper Association
cu	colour units
$D_{\varnothing}$	first chlorine dioxide bleaching stage (0 % chlorine)
D_n	neutralized chlorine dioxide brightening stage
d	day
E	alkaline extraction stage
EIA	environmental impact assessment
EMCC	extended modified continuous cooking
E_o	oxygen-reinforced alkaline extraction stage
E_{op}	oxygen- and peroxide-reinforced alkaline extraction stage
F/M	food to microorganism ratio
g	gram
h	hour
H/W	hardwood
ISO	International Standards Organization
kg	kilogram
L	liter
MCC	modified continuous cooking
m	meter
m^2	square meter
m^3	cubic meter
mg	milligram
N	nitrogen
ng	nanogram
P	phosphorus
POX	purgeable organic halogen
pg	picogram
ppm	parts per million
ppb	parts per billion
ppt	parts per trillion
ppq	parts per quadrillion
s	second
SRT	solids retention time
S/W	softwood
TCDD	tetrachloro-dibenzo-para-dioxin
TCDF	tetrachloro-dibenzofuran
TCDD/F	tetrachloro-dibenzo-para-dioxin and furan
TMP	thermo-mechanical pulping
TSS	total suspended solids
%	percent
µg	microgram

Section 1—Introduction

1.1 Historical Context

Alberta-Pacific Forest Industries Inc. ("Alberta-Pacific") proposes to build and operate a bleached kraft pulp mill in the County of Athabasca No. 12, near the Town of Athabasca (Figure 1.1.1). The proposed mill would utilize hardwood and softwood forest resources. It would have nominal production capacities of 1500 air dried metric tonnes per day (ADt/d) of hardwood pulp or 1250 ADt/d of softwood pulp. Alberta-Pacific projects that in the long term, 79% of the annual production would be hardwood pulp.

An Environmental Impact Assessment review process was undertaken pursuant to an agreement between the Alberta and federal Ministers of the Environment dated July 11, 1989. That agreement called for the establishment of a joint provincial-federal public review of the environmental impacts of the proposed pulp mill.

The particulars of the hearing process conducted by the Alberta-Pacific Environmental Impact Assessment Review Board (the "Review Board") are set out in detail in the Review Board's report dated February 28, 1990. Certain portions of the Review Board's report bear repeating in order to place the task of the Alberta-Pacific Scientific Review Panel (the "Panel") into context. These relate to the subject of chlorinated organic compounds.

The Review Board described the basic concerns over chlorinated organic compounds as follows:

> "Chlorinated organic compounds have been of widespread public concern for over two decades..... Some are extremely toxic, and some are both persistent in the environment and biomagnified as they are passed up food chains....
>
> "Of concern with respect to pulp mills are dioxins, furans, chlorinated phenols, and 300 to 1,000 other chlorinated organic compounds....
>
> "The presence of dioxins and furans, two of the most toxic types of chlorinated organic compounds, was first discovered in the effluents of bleached kraft pulp mills in 1985. The compounds have been found in the effluents of most older mills of this type, as well as in receiving waters below almost all older bleached kraft mills. The source of these compounds and most other organochlorines was discovered to be the chlorine bleaching process, where high concentrations of lignin and other organic materials dissolved from wood fibre are exposed to high concentrations of chlorine. Some defoaming agents were also implicated, but have since been eliminated by the industry. Since the discovery of dioxins and furans in effluents of bleached kraft pulp mills, the pulp and paper industry has made great progress in reducing their formation by using oxygen delignification, extended pulp cooking, substitution of chlorine dioxide for chlorine in the bleaching process and by more complete secondary treatment of effluents before discharging them to natural waters." (EIA Review Board, 1990a)

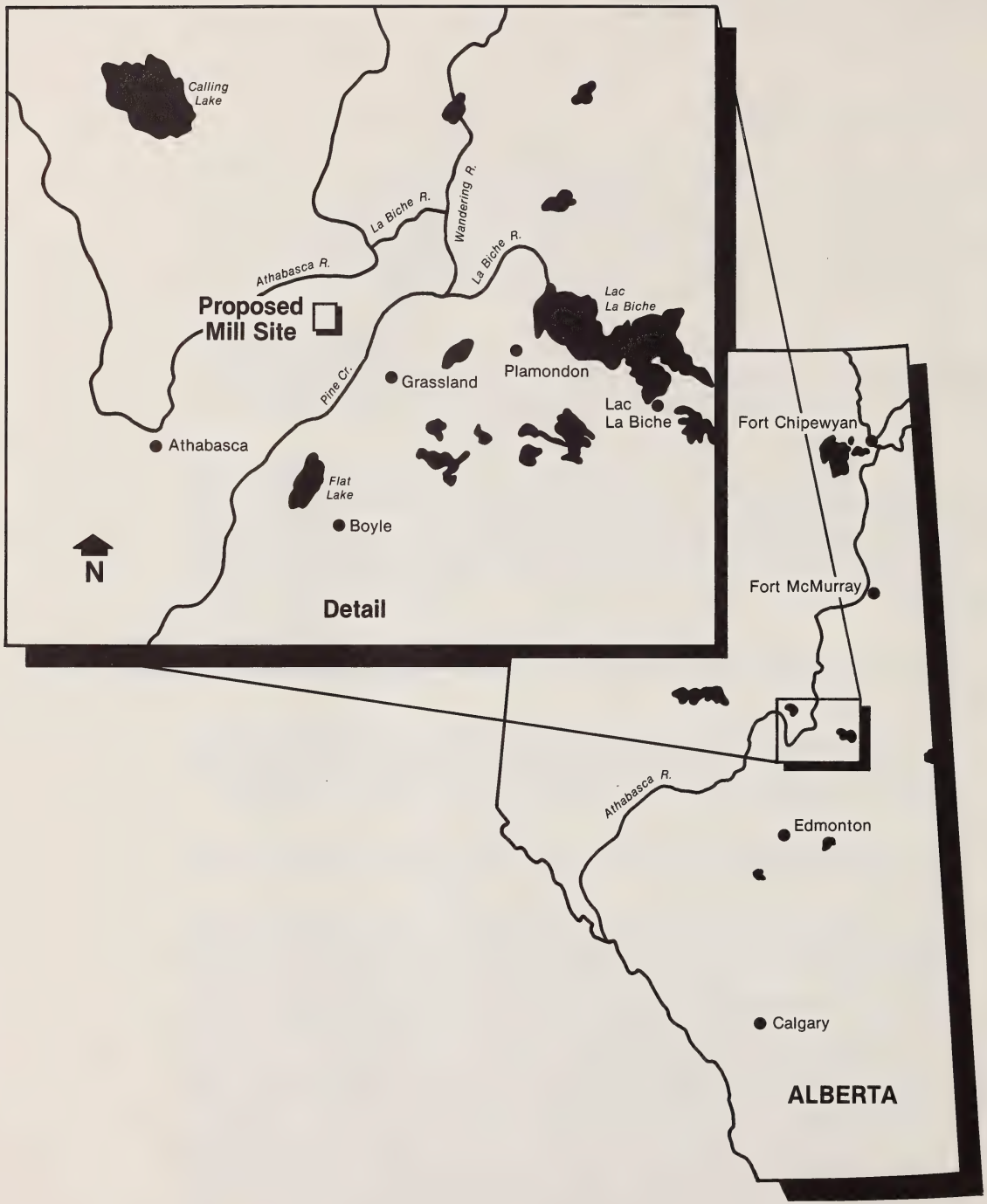


Figure 1.1.1 Proposed Location of Alberta-Pacific Mill. (EIA Review Board, 1990).

After discussing matters such as the toxicity, bioaccumulation and persistence of chlorinated organic compounds, their presence in the Athabasca and Peace River systems, and assessing the Alberta-Pacific proposal, the Review Board made the following conclusion (among others).

> "The mill proposed by Alberta-Pacific would be a very modern one, discharging less chlorinated organic compounds per tonne of pulp produced than any other mill in Canada, and perhaps in the world. However, due to the large capacity of the mill and the relatively small volume of the Athabasca River, the mill could contribute significantly to the already elevated concentrations of chlorinated organic compounds." (EIA Review Board 1990b)

Based on that finding, the Review Board recommended that the project not be allowed to proceed until a number of further environmental studies were completed that would establish the origin and degree of contamination in the area river systems. The Review Board also recommended that existing discharges of chlorinated organic compounds be decreased as rapidly as practical.

Following the Premier's directive at the public release of the Review Board's report, the Alberta Government commissioned a complementary scientific review of the Alberta-Pacific proposal by the Finnish consulting firm of Jaakko Pöyry Oy. The purpose of that analysis and the ensuing report dated June 29, 1990 was to study the earlier EIA and find complementary scientific and technical data to better assess the potential and probable environmental effects of the proposed development. The Jaakko Pöyry report compared the proposed Alberta-Pacific mill to other pulp mills in operation in Alberta and other major pulp producing areas of the world. It made its own assessment of future environmental impacts, human health effects and of impacts on fish and fisheries. It analyzed the spatial extent of environmental impacts in the study area, and formulated conclusions regarding the potential for ecotoxicological and human health effects.

After releasing the Jaakko Pöyry report, the Alberta Minister of the Environment announced, together with the federal Environment Minister, an agreement to study the cumulative impact of development on the Northern Rivers including the Peace, Athabasca and Slave River systems and their tributaries, as recommended by the Review Board.

The Minister also announced a number of other responses by the Alberta Government to the Review Board's recommendations, including the commissioning of various additional studies and the initiation of a number of public consultation programmes.

On July 12, 1990, the Minister of the Environment also announced the establishment of this three person panel to review new technology proposed by Alberta-Pacific for the mitigation of discharges of chlorinated organic matter into the Athabasca River.

This new technology and proposal were alluded to, in general terms, in the Jaakko Pöyry report, but at the time of writing of that report, remained unavailable. Therefore, the Jaakko Pöyry report merely discussed methods known to its authors for reduction of chlorinated organics to levels below those originally proposed by Alberta-Pacific (i.e. 1.3 kg/ADt; Jaakko Pöyry, 1990).

1.2 Terms of Reference

The Ministerial Order establishing this Scientific Review Panel sets out terms of reference as follows:

> "The Terms of Reference of the Review Panel shall be to inquire into and advise the Minister of the Environment on the improvements proposed by Alberta-Pacific Forest Industries Inc. to the wood-pulping and bleaching process as they relate to the mitigation of the discharge of chlorinated organics into the Athabasca River". (Appendix 1)

The improvements referred to in the Ministerial Order are described in a document entitled "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds", prepared by Alberta-Pacific, Beak Consultants Ltd. and H.A. Simons Ltd. (The "Mitigative Response"). This report was provided to the Minister of the Environment under covering letter dated July 5, 1990. It was released to the public on July 6, 1990. In the Executive Summary of the Mitigative Response, Alberta-Pacific stated:

> "Alberta-Pacific has examined in detail the Review Board's concerns related to chlorinated organics. It was felt that a strong positive response was required to address public concern. Alberta-Pacific and their consultants conducted an intensive study of the proposed pulping and bleaching technology. As a direct result of this technical review, it was determined that operating refinements could be made to the fibreline. These refinements form the basis of the mitigative measures outlined in this report."

> "The key to Alberta-Pacific's mitigation proposal is the operation of the Kamyr MCC digester. Operation using the modified pulping equipment included in the original mill design in an extended MCC mode has been proven to delignify to a 10-12 kappa level on hardwood. The combination of extended cooking with the fully proven technique of oxygen delignification results in a very low kappa to the bleach plant. The low kappa makes possible the elimination of molecular chlorine gas from the bleaching process.

> "The chlorine gas free bleaching strategy coupled with the reinforcement of the extraction stage with hydrogen peroxide significantly reduces the concentration of AOX in the mill effluent, while maintaining pulp quality. The proposed Alberta-Pacific fibreline will achieve AOX levels of less than 0.25 kg/ADt of pulp. At this level the Alberta-Pacific mill would be the smallest contributor on the Athabasca/Peace/Slave River system, representing 10 percent of the 1990 Alberta regulatory AOX levels referenced by the Review Board." (Alberta-Pacific *et al.*, 1990; original emphasis.)

The Panel's mandate required that two fundamental issues be addressed. First, the Panel must assess whether the revised proposal is technically feasible. That is, is it possible to design, construct and operate a bleached kraft pulp mill as proposed by Alberta-Pacific? Secondly, it must assess the quantities and characteristics of the chlorinated organic matter expected to be discharged from the Alberta-Pacific mill.

The Panel did not believe that the Terms of Reference required or authorized it to review and advise the Minister as to the veracity of all of the information and claims included in the Mitigative Response.

In particular, the Panel has not made any assessment of portions of that document which deal with the toxicity of AOX, nor has it assessed claims made by Alberta-Pacific to be able to achieve "environmental harmony" with its modified proposal. While important, such subjects do not fall within the Panel's Terms of Reference.

1.3 Investigations and Advisors

The Panel used several methods in gathering scientific and technical information on the proposed pulping and bleaching technology, including the following:

- The Panel advertised a solicitation of scientific and technical submissions from the public.

- The Panel commissioned submissions from recognized scientific and technical professionals including:

  Mr. Neil McCubbin (private engineering consultant, Foster's Point, Quebec)
  Mr. Ed Barnes (private engineering consultant, Burnaby, British Columbia)
  Dr. Kyosti Sarkanen (University of Washington, Seattle)

- The Panel engaged the following staff experts:
  Dr. Douglas Reeve (Pulp and Paper Centre, University of Toronto)
  Dr. Harald Thimm (private consultant, Calgary)

- Within the time frame available, the Panel and its staff carried out their own investigations and arranged briefings, field trips and interviews with specialists in the pulp and paper area.

- A Workshop was held.

The Panel received technical briefings from two consultants having expertise in the pulp and paper area. Along with one of its technical experts, and representatives of the British Columbia Environment Ministry, it also visited a pulp mill owned and operated by Crestbrook Forest Industries in southeastern British Columbia, which employs some of the technology slated to be used in the proposed Alberta-Pacific mill. For similar reasons, the Panel asked one of the technical professionals (Mr. Ed Barnes) to visit the Longview Fibre Company mill in the State of Washington, U.S.A., and to report on the operating experience with the Kamyr digester. Finally, one of the Panel's staff experts (Dr. D. Reeve) was requested to discuss the operation of the Kamyr digester in two Scandinavian mills referred to in the Mitigative Response, with Swedish technical experts during the course of an unrelated trip to Finland.

1.4 Submissions Received

Prior to the commencement of the September 12, 13 and 14 Workshop in Athabasca, the Panel had received 23 submissions, two of which were requested of technical experts the Panel had contacted. Submissions were also received during the Athabasca Workshop. A total of 55 submissions was received by the Panel.

The content of the submissions varied widely, with a considerable number focussing on the impacts on the environment of any effluent or emission, which issues are beyond the Terms of Reference. For example, the Department of Fisheries and Oceans erroneously interpreted the definition of the Terms of Reference to mean "the Review Panel will consider the effectiveness of the proposed mitigation measures in reducing potential impacts on fish and fish habitat" (Department of Fisheries and Oceans, 1990). Mr. John McInnis, M.L.A. observed that "there is new evidence of organic chloride contamination of fish on the Peace and Athabasca Rivers" (McInnis, 1990). Others expressed concern about "the continuing push towards the depletion of our forest base here in the province of Alberta" (Parker, 1990). The projected site of the plant was of continuing concern to persons such as Mr. Peter Opryshko, who spoke at the Workshop and is a resident of the Prosperity area.

In addition, a number of submittors took issue with several aspects of the review, including:

- the narrowness of the Terms of Reference,
- the shortness of the time for preparation and the inappropriate time of the year,
- the independence of the panel,
- the difficulty of obtaining independent scientific and technical assistance, and
- the difficulty of accessing some of the documents and references required for the review.

Others, within the limitations imposed on them by the time constraints and by the difficulty in finding scientists with appropriate background, did make submissions containing relevant material. The Panel sought augmentation of several of these at the Workshop.

1.5 Submissions Presented for Augmentation/Clarification

By August 29, 1990 the Panel had reviewed all submissions received at that time and had decided on those it wished to have augmented at the Workshop. The Panel provided two locations in Edmonton and one in Athabasca where the public and the media could examine the submissions or make copies for their own use.

The Panel reviewed all submissions to determine their relevance, having regard for the Terms of Reference. In acknowledging receipt of the submissions, the Panel advised that all submissions, irrespective of content, would ultimately be made available to the Minister of Environment. The criteria for selection for augmentation were straightforward. The submission had to be relevant to the Terms of Reference and had to require, in the opinion of the Panel, further clarification.

1.6 The Athabasca Workshop

Having selected a number of submissions for presentation at the Athabasca Workshop, the Panel adopted procedures for the session which were somewhat similar to those used in scientific conferences. The agenda for the Workshop is set out in Appendix 2. During the course of the three day proceeding, the Panel heard from a very broad range of participants, and afforded all interested parties an opportunity to question presenters and to comment on Alberta-Pacific's Mitigative Response.

1.7 References

Alberta-Pacific Environmental Impact Assessment Review Board (1990). "The Proposed Alberta-Pacific Pulp Mill: Report of the EIA Review Board". February 28, Edmonton, Alberta. (a) p. 21, (b) p. 31-32.

Alberta-Pacific Forest Industries Inc., Beak Consultants Ltd. and H.A. Simons Ltd. (1990). "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds". Submission No. 46 to The Alberta-Pacific Scientific Review Panel, September 14, Edmonton, Alberta, p. S-1.

Department of Fisheries and Oceans (1990), "Submission to the Alberta-Pacific Review Panel Concerning the Alberta-Pacific Report Entitled Mitigative Response to Concerns Regarding Chlorinated Organic Compounds". Submission No. 10 to The Alberta-Pacific Scientific Review Panel, August 23, Edmonton, Alberta, p. 2.

Jaakko Pöyry Oy (1990) "Complementary Scientific Review of the Proposed Alberta-Pacific Pulp Mill Project Environmental Impact Assessment: Main Report". Alberta Research Council, ARC Contribution Series 1855, June, Edmonton, Alberta, p. 8.

McInnis, John, MLA (1990) "Top Ten Reasons Why Alberta-Pacific Forest Industries Should Not Now be Licensed for Construction Submission to Al-Pac II Scientific Review Panel." Submission No. 15 to The Alberta-Pacific Scientific Review Panel, August 22, Edmonton, Alberta, p. 3.

Parker, David J. (1990) Letter and attachments directed to the 2nd Al-Pac Review Panel. Submission No. 17 to The Alberta-Pacific Scientific Review Panel, August 10, Edmonton, Alberta, p. 1.

Section 2—Preface to the Scientific Review

2.1 The Scope of the Panel's Review

The Terms of Reference directed the Panel to examine the process changes in the revised fibreline that are purported to mitigate chlorinated organic material discharges; namely the extended modified continuous cooking, the 100% chlorine dioxide substitution plus an additional D_n stage and the hydrogen peroxide addition to the E_o extraction stage. The proposed changes in these elements of the fibreline will result in changes elsewhere in the overall mill process. For example, the lowering of the pulp kappa number before bleaching may result in more unchlorinated lignin degradation products entering the chemical recovery cycle. Details of such secondary changes were not presented in the Mitigative Response. However, where data were available, the Panel considered them as part of the assessment. Systems such as the wood chip and final product (pulp) preparation, that will not change as a result of the revised fibreline were excluded from consideration on the assumption that these have been adequately assessed by the Review Board.

Questions referred to the Panel by public participants relating to the chemistry of bleaching with chlorine dioxide, the analytical chemistry of bleaching effluents and the production of chlorate were considered during the Panel's deliberations. Other matters, such as environmental fate and impact of chlorinated organic material discharges were, as mentioned earlier, judged to be beyond the Panel's mandate.

In its review, the Panel examined all of the information available to it, and where possible, attempted to define expected rates of organochlorine discharge at specified levels of confidence. The Panel did not attempt to determine whether these expected organochlorine discharge rates were acceptable. Such considerations clearly fall outside of the Panel's Terms of Reference.

2.2 Science Versus Industrial Design

The Terms of Reference required the Panel to inquire into and report on the industrial process design modifications described in the Mitigative Response. Those modifications are not based on pure experimental science. Nor can they be. They are based on an evolving empirical understanding of applied industrial processes.

In this context, it was somewhat unfortunate that a number of submissions, presentations and comments at the Athabasca Workshop appeared to reflect a degree of confusion as to the standards which ought to be applied in evaluating the Mitigative Response. The lack of peer-reviewed, published, scientific analysis of the physics and chemistry of pulping and bleaching processes was taken as an indictment of the industry's ability to perform, when in fact, it should be understood as being a product of a competitive industrial environment.

Industrial designers do not need to fully understand why a process functions. They must however, be confident that it will function. Although such confidence can be aided by a

good understanding of the underlying physics and chemistry, real confidence can only come from the successful implementation of an industrial design. Therefore, industrial designers rely more on industrial scale empirical evidence, than on rigourous scientific analysis of the underlying process fundamentals.

It must also be recognized that the purpose of science is not only to generate knowledge using a rigourous set of protocols, but also to disseminate this knowledge through peer-reviewed publications. Good industrial process development is predicated upon the use of comparably rigourous techniques. However, dissemination of the resulting information is not usually an industrial objective. For competitive reasons, industrial designers may actually prefer not to make data available for review. At the very least, industrial designers may not have the luxury of sufficient time to prepare and present technical documentation for public review.

As mentioned earlier, the Panel's mandate was to inquire into and report on two fundamental issues: the technical feasibility of the revised process, and the expected effluent characteristics. These are largely questions of science within the context of industrial design and this report has been prepared accordingly.

Section 3—The Revised Pulp Mill Proposal

3.1 Description

The most complete description in the public record of the proposed mill is contained in the original environmental impact assessment (EIA) report submitted to the Alberta Environment Minister by Alberta-Pacific on May 8, 1989 (Alberta-Pacific, 1989a). Two subsequent reports provided supplemental information requested by Alberta Environment pursuant to its internal review of the EIA (Alberta-Pacific, 1989b) and a revised proposal for the mill effluent treatment system (Alberta-Pacific, 1989c). Abbreviated descriptions of the proposed mill also appear in the EIA Review Board (1990) report and in the report prepared by Jaakko Pöyry (1990).

The Mitigative Response (Alberta-Pacific *et al.*, 1990a) describes changes to the original fibreline and associated chemical systems for the purpose of reducing (mitigating) the discharge of chlorinated organic materials from the proposed mill without adversely affecting the quality of the pulp produced. Figure 3.1.1 of this report illustrates the revised fibreline and indicates where revisions have been made.

The mill would be designed to produce a nominal average 1500 ADt/d of hardwood pulp for 260 days per year and 1250 ADt/d of softwood pulp for 85 days per year (Alberta-Pacific, 1989a; p. 2.1). For the first two years of operation, only hardwood pulp would be produced (Fenner, Transcript, p. 569). The hardwood would be primarily aspen poplar, with up to 15% balsam poplar. After the first two years of operation, the softwood would be primarily white spruce with some jackpine, black spruce and balsam fir (Alberta-Pacific, 1989a; p. 2.1). Alberta-Pacific contemplates hardwood/softwood campaigns consisting of approximately 21 days of hardwood followed by 8 days of softwood (Fenner, Transcript, p. 570).

In the revised fibreline, extended modified continuous cooking (EMCC) replaces modified continuous cooking (MCC), illustrated at A in Figure 3.1.1. The remaining steps in the pulping process are unaltered. The revised bleaching sequence incorporates the following changes:

1) the chlorine dioxide substitution is increased from 70% to 100% (B in Figure 3.1.1, "chlorine-free bleaching");

2) hydrogen peroxide is introduced into the oxygen-reinforced caustic extraction stage (E_{op}) and the temperature and pressure are increased (C in Figure 3.1.1); and

3) an additional chlorine dioxide brightening stage, D_n, is added (D in Figure 3.1.1). There are no facilities for utilizing molecular chlorine in the bleach plant in the revised proposal (Fenner, Transcript, p. 617).

All other processes in the mill, including the chemical recovery, power generation, chip preparation, water and wastewater treatment and product (pulp) preparation for shipment, remain unchanged. The target product (pulp) quality specifications also remain unchanged.

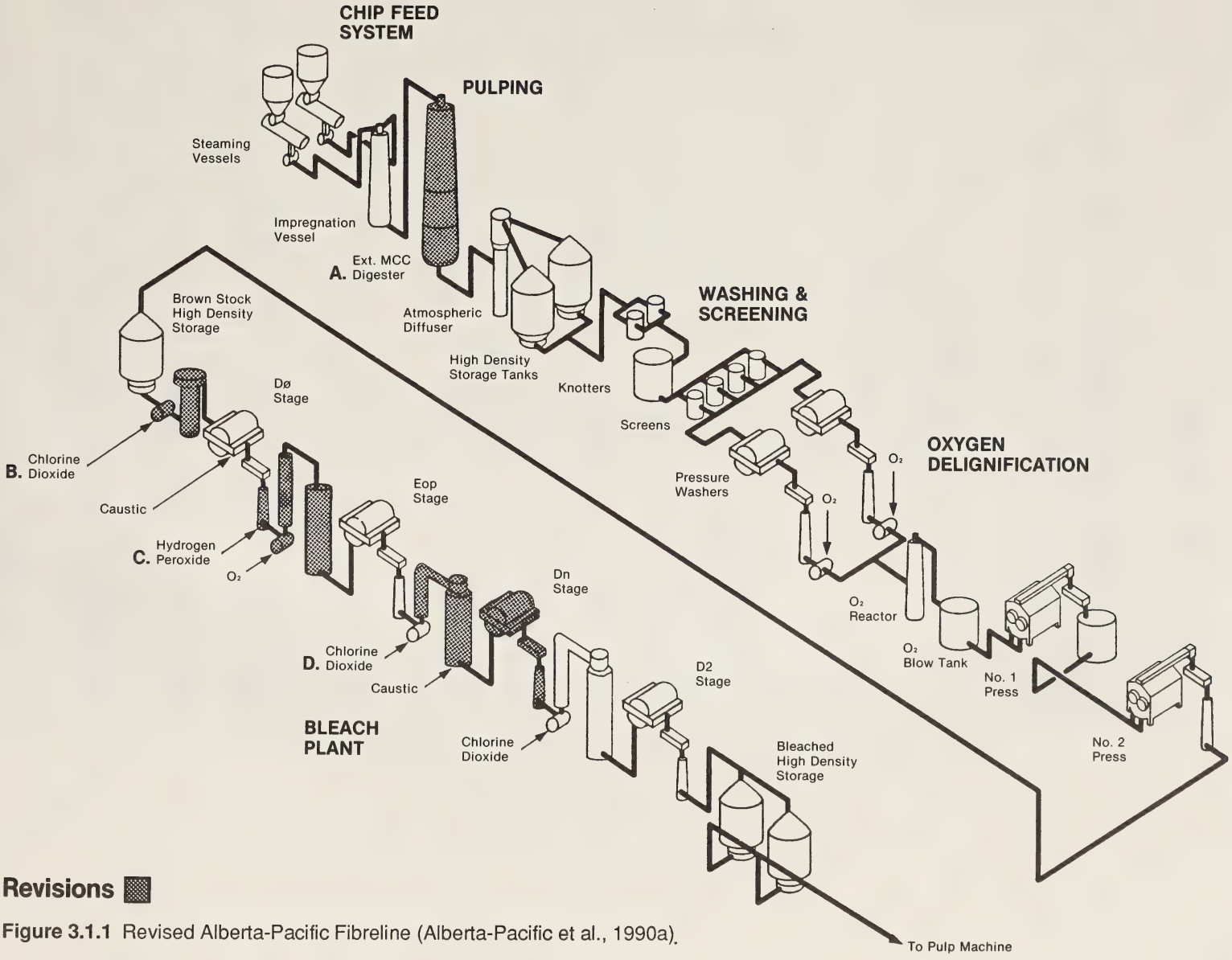


Figure 3.1.1 Revised Alberta-Pacific Fibreline (Alberta-Pacific et al., 1990a).

Revisions

3.2 Quantitative Changes

As a result of the fibreline changes proposed, various parameters relating to the discharge of chlorinated organic materials have changed. Alberta-Pacific's estimates of those changes are summarized in Table 3.2.1. The upper portion of the table contains the pulp production and chemical consumption figures and the lower portion contains the effluent discharge targets.

Table 3.2.1
Comparison of Parameters
in the Original and Revised Proposed Fibrelines
(Nominal Capacity)

Parameter		Original Value	Revised Value	Reference
Hardwood Pulp Production		1500 ADt/d	1500 ADt/d	(1, p. 119)
Softwood Pulp Production		1250 ADt/d	1250 ADt/d	(2, p. 567)
Molecular Chlorine	(a)	9.1 t/d	0.15 t/d	(est. by Panel)
Consumption (in bleaching)	(b)	1.9 t/d	No new value offered	
Chlorine Dioxide	(a)	20.6 t/d	15.1 t/d	(est. by Panel
Consumption	(b)	23.7 t/d	No new value offered	from 1, p. 90)
Sodium Hydroxide	(a)	17.8 t/d	11.8 t/d	(1, p. 90)
Consumption	(b)	22.4 t/d	No new value offered	
Sulphuric acid	(a)	4.2 t/d	19.4 t/d	(1, p. 90)
Consumption	(b)	4.0 t/d	No new value offered	
Effluent Flow		82,060 m^3/d	60,480 m^3/d	(1, p. 126)
BOD_5 produced	(c)	37.5 t/d	24.0 t/d	(1, p. 126)
BOD_5 discharged	(c)	2.25 t/d	1.5 t/d	(1, p. 126)
Suspended Solids produced	(c)	39.0 t/d	No new value offered	
Suspended Solids discharged	(c)	4.5 t/d	4.5 t/d	(3, p. 6)
AOX produced	(c)	2.1 t/d	0.59 t/d	(est. by Panel
AOX discharged	(c)	1.5 t/d	0.32 t/d	from 4, p. 1 & 2)
Colour discharged	(c)	63 t/d	No new value offered	
Chlorate produced	(c)	4.8 - 5.6 t/d	2.9 - 7.2 t/d	(est. by Panel
Chlorate discharged	(c)	No value offered	0.3 - 0.72 t/d	from 2, p. 582)

Notes: (a) = Hardwood
(b) = Softwood
(c) = Long term average (79% hardwood + 21% softwood).

(1) Alberta-Pacific *et al.* (1990a)
(2) Transcript of Athabaca Workshop
(3) Alberta-Pacific (1989c)
(4) Alberta-Pacific *et al.* (1990b)

3.3 Revised Fibreline Treated Effluent Characteristics

Alberta-Pacific claims that the revised fibreline will produce an effluent for discharge into the Athabasca River that has characteristics summarized in Table 3.3.1.

Table 3.3.1

Revised Fibreline Mill Treated Effluent Characteristics
(Long-term average values)

Parameter	Production Rate Per ADt of Pulp	Daily Discharge Rate	Concentration in Final Effluent
Flow	40.3 m^3	60,480 m^3	Not applicable
BOD_5	1.0 kg	1500 kg	25 mg/L (ppm)
TSS	3.0 kg	4500 kg	75 mg/L (ppm)
AOX	0.22 kg	320 kg	5.3 mg/L (ppm)
Colour	42.0 kg	63000 kg	913 cu
Total Resin Acids [b]	319.4 mg	479 g	7.9 µg/L (ppb)
Total Chlorinated Phenols [b]	18.5 mg	27.8 g	460 ng/L (ppt)

Notes: [a] Colour units
[b] These values are for hardwood only.

The data contained in Table 3.3.1 have been extracted from three sources; the Mitigative Response (Alberta-Pacific *et al.*, 1990a), Becker and Holloran (1990) and Stanley Associates (1989).

The data from these three sources are not consistent and clearly represent an evolving design situation. For example the flow rate estimate has been variously quoted as 1.0 m^3/s, 0.8 m^3/s and 0.7m^3/s and the effluent BOD_5 concentrations corresponding to those flows have been given as 27 mg/L, 26 mg/L and 25 mg/L. While these differences may seem insignificant, in various combinations they could reflect a reduction of 33% in the daily BOD_5 mass discharge to the Athabasca River.

Alberta-Pacific also claims that the tetrachlorinated dioxins and furans discharge levels in treated effluent will be less than 2 pg/L (2 ppq). This issue is reviewed in more detail in Section 5.3 of this report.

3.4 The Toxicity of Chlorinated Organic Compounds in Revised Fibreline Treated Effluent

A considerable portion of the Mitigative Response presents information suggesting a dramatic reduction in the toxicity of the revised fibreline treated effluent. Alberta-Pacific's estimate of the reduction of the chlorinated organic material discharge in the effluent suggests a parallel toxicity reduction. However, as was argued in one submission (Fisheries and Oceans, 1990), the degree of toxicity depends upon the speciation, as well as the concentration of the chlorinated organic constituents of the effluent. Until larger quantities of effluent are available from the revised fibreline, it will not be possible to measure the toxicity of the Alberta-Pacific effluent. A detailed consideration of the proponent's toxicity claim was judged to be beyond the Terms of Reference in the Ministerial Order.

3.5 References

Alberta-Pacific Environmental Impact Assessment Review Board (1990). "The Proposed Alberta-Pacific Pulp Mill: Report of the EIA Review Board". February 28, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc. (1989a) "Alberta-Pacific Forest Industries Inc. Environmental Impact Assessment: Bleached Kraft Pulp Mill Main Report". May 8, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc. (1989b). "Alberta-Pacific Forest Industries Inc. Environmental Impact Assessment: Supplemental Information". September 8, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc. (1989c) "Mill Effluent Treatment System: Activated Sludge Process". October, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc., Beak Consultants Ltd. and H.A. Simons Ltd. (1990a). "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds". Submission No. 46 to The Alberta-Pacific Scientific Review Panel, September 14, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc., Beak Consultants Ltd. and H.A. Simons Ltd. (1990b). "Errata to Alberta-Pacific Mitigative Report". Submission No. 46.1 to The Alberta-Pacific Scientific Review Panel, September 14, Edmonton, Alberta.

Becker, E. and M. Holloran (1990). "Alberta-Pacific Lab Scale Pulping and Bleaching Trial B-1444-1". Submission No. 31 to The Alberta-Pacific Scientific Review Board, September 13, Athabasca, Alberta.

Department of Fisheries and Oceans (1990). "Submission to the ALPAC Scientific Review Panel Concerning the ALPAC Report Entitled Mitigative Response to Concerns Regarding Chlorinated Organic Compounds". Submission No. 10 to the Alberta-Pacific Scientific Review Panel, August 23, Edmonton, Alberta.

Jaakko Pöyry Oy (1990). "Complementary Scientific Review of the Proposed Alberta-Pacific Pulp Mill Project Environmental Impact Assessment: Main Report". Alberta Research Council, ARC Contribution Series 1855, June, Edmonton, Alberta, p. 9-29.

Stanley Associates Engineering Ltd. (1989). "Alberta-Pacific Forest Industries Inc. Pulp Mill Effluent Treatment Plant 3605-d, AREA 17: Pre-Design Report". Job. No. 71-194-01-09, Alberta-Pacific Forest Industries Inc., November, Edmonton, Alberta.

Section 4—Technical Feasibility of Revised Pulping and Bleaching Processes

This section of the report considers the feasibility of the revised pulping and bleaching technologies proposed by Alberta-Pacific. In making its assessment, the Panel sought to determine whether it is possible to design, construct and, in particular, operate a bleached kraft pulp mill which incorporates extended modified continuous cooking (EMCC), oxygen delignification, and molecular chlorine-free bleaching with an integral oxygen- and peroxide-reinforced alkaline extraction stage.

4.1 Extended Modified Continuous Cooking (EMCC)

The revised fibreline proposal prepared by Alberta-Pacific and its engineering consultants provides an extensive background summary of the current state of knowledge on alkaline pulping (Alberta-Pacific *et al.*, 1990; Chapter 2.1). The content of this section was generally accepted in testimony from Dr. R. Berry (PAPRICAN, 1990) and Dr. K. Sarkanen (1990) of the University of Washington. The Panel and its technical advisors also reviewed the material and found it to be consistent with the generally-accepted state of knowledge as described in standard pulping technology textbooks such as Casey (1983) and Grace *et al.* (1989). The Panel therefore accepts the validity of the background material presented in Chapter 2.1 of the Mitigative Response.

The two-vessel hydraulic digester proposed in the Mitigative Response is shown for reference in Figure 4.1.1. The digester height has been increased beyond that of the original proposal in order to provide increased retention time in the counter-current wash zone. The diameter of the bottom section of the digester has also been increased. The extended MCC design also incorporates an additional white liquor addition point in the counter-current wash zone and the heaters associated with the counter-current wash zone have been upgraded to permit higher temperature operation. A future possible modification, referred to in the text of the Mitigative Response, but not illustrated on Figure 4.1.1, allows for the addition of black liquor prior to the impregnation vessel.

The sub-sections which follow, provide the Panel's review of the extended modified continuous cooking EMCC system. The review focusses on five issues:

1) the extent of delignification,

2) the strength of the pulp,

3) the pulp yield,

4) the runnability or operability of the process, and

5) the likely effects of the EMCC on downstream pulp processing.

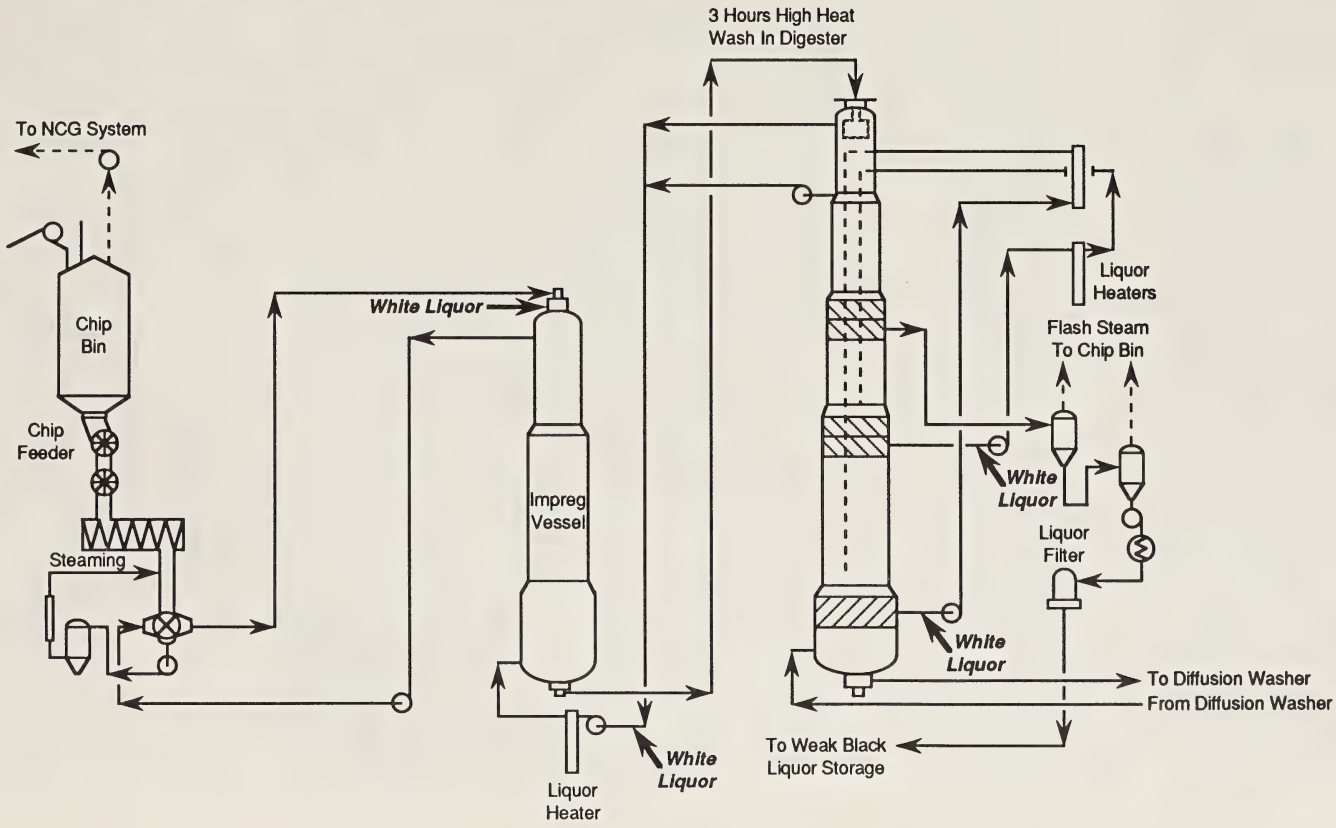


Figure 4.1.1 Extended Modified Continuous Cooking (EMCC) System (Alberta-Pacific et al., 1990).

4.1.1 Extent of Delignification

The overall purpose of the EMCC digester design shown in Figure 4.1.1 is to provide a less aggressive, but more extended cooking of the pulp. This is to be accomplished by equalizing the digester alkali concentration to the greatest extent possible and by maintaining a low dissolved lignin concentration at the end of the cook. These conditions have been selected to produce hardwood and softwood pulps with low kappa numbers so that reduced amounts of lignin will be passed to the bleach plant, in order to mimimize the formation of chlorinated organic matter. PAPRICAN (1990) summarized mill scale data which indicate that the minimum kappa numbers attained to date in the EMCC system are 8 for hardwood and 16 for softwood.

At the Athabasca Workshop, Dr. Berry (PAPRICAN, 1990) and Dr. Sarkanen (Transcript, p.101) stated that for hardwood, kappa 10 is easily attained in an EMCC digester system. In his written submission Dr. Sarkanen contended that "the rather conservative targeted kappa range of 10 to 12 ought to be possible to reach without extensive charge of white liquor to the counter-current zone of the digester" (Sarkanen, 1990). Dr. Berry presented a compilation of anecdotal data collected by several PAPRICAN staff members during visits to mills. The specific mills visited and the nature and quality of the data thus obtained were not presented. The results summarized by PAPRICAN (1990) indicate that mill experience suggests that after extended pulping, aspen pulp kappa numbers of between 8 and 13 might be reasonably expected. For softwood, the comparable figures would be 16 and 26.

Only a few additional corroborating data were presented to the Panel. In a site visit report commissioned by the Panel (Barnes, 1990), Mr. E. Barnes confirmed that the Longview Fibre Company operates an MCC digester for softwood pulping. It should be noted that the MCC system is a predecessor to the EMCC system proposed by Alberta-Pacific. Operating summary data provided by Longview indicate that production runs have been completed in which softwood was pulped to kappa numbers as low as 9. It was pointed out by several participants at the Workshop that the lower initial lignin content of aspen should enable even lower kappa numbers to be attained in an MCC system. Laboratory aspen pulping studies reviewed by Greenwood (1988) confirmed that MCC hardwood pulps could be delignified to 6 kappa. A corroborating datum was provided by Dr. E. Becker during his description of the methodology followed in a bleaching trial on EMCC aspen pulp. Aspen chips taken from the Athabasca area were cooked in a laboratory pilot plant under conditions which would "simulate...the results that are obtained in pulp mills" (Transcript, p. 273). The resulting aspen pulp kappa number measured was 8.9 (Becker and Holloran, 1990).

4.1.2 Pulp Strength

The Panel recognizes that pulp strength is a less critical parameter for a hardwood pulp such as aspen, than for a softwood pulp. Hardwood pulps are used primarily for providing good formation, a good printing surface and opacity. Strength in the final sheet is usually obtained by blending a stronger softwood pulp with the desired amount of hardwood pulp.

In a technical review compiled by Kamyr Inc. (Greenwood, 1988), laboratory studies of the MCC pulping process with aspen indicated that burst factor, tear factor and tensile

strength of MCC aspen pulp were not significantly reduced when cooking was continued to kappa numbers as low as 6. Limited comparative data at kappa numbers between 15 and 19 suggested that the MCC pulps exhibited better strength characteristics than aspen pulped in a conventional co-current digester mode. Mill scale MCC pulping results were reported by both Greenwood (1988) and Barnes (1990). Greenwoood reported that softwood pulped in the MCC mode showed between 10% and 30% improvement in observed tear at a given tensile level. Barnes indicated that the Longview Fibre mill utilizes MCC pulping specifically to improve the strength of its softwood pulp. The strength of this softwood pulp is maintained at kappa numbers as low as 9. A similar report has been published recently by Whitley *et al.* (1990).

The Panel notes that is difficult to extrapolate from the limited data available on MCC pulping to the EMCC digester proposed by Alberta-Pacific. All evidence presented from the MCC process indicates better pulp strength with both hardwood and softwood pulping. Further, due to the limited importance placed on hardwood pulp strength, and since 79% of the mill output would be hardwood pulp, the Panel feels that Alberta-Pacific pulp strength should not be materially affected by the use of EMCC pulping to extended delignification levels.

4.1.3 Pulp Yield

The issue of pulp yield in the EMCC digester was an area of concern to some submittors. It was noted by Sarkanen (1990) that "potential pulp yield loss...may limit the application of...partial counter-current pulping and white liquor addition to the hi-heat washing zone". Greenwood (1988) reported that the laboratory MCC aspen pulping trials demonstrated a decrease in pulp yield as the final kappa number was extended from 18 to 6. Barnes (1990) reported that Longview Fibre utilized a solids balance around the full scale softwood MCC digester to monitor yields at various degrees of cooking. Recent data from Longview suggests that there may be "an accelerated drop off in yield...around 15 kappa number for softwood pulps" (Barnes, 1990). A visual inspection of the data from Longview, makes it apparent that this conclusion had been based on what appears to be one spurious point at kappa 16 and two points at kappa 17-18 which suggest some deviation from the normal Hatton kappa-yield relationship. The Panel agrees that some yield loss may accompany extended MCC pulping. The Panel also recognizes that the primary impact of yield loss may be its negative effect on process economics. If the economic impact becomes excessive, Alberta-Pacific could ameliorate yield loss by operating the digester at higher kappa numbers. Dr. Berry (PAPRICAN, 1990) concluded that "even without the benefit of EMCC, the combination of MCC and oxygen delignification alone could be used to pulp aspen to the levels proposed by Alberta-Pacific". This suggests that some flexibility is available to counteract yield loss by cooking to higher kappa numbers without increasing the amount of lignin ultimately passing to the bleach plant.

4.1.4 Digester Runnability

Due to the limited operating experience with extended MCC pulp digesters, it is difficult to comment directly on EMCC runnability. However, a few anecdotal reports on MCC runnability were submitted for the Panel's consideration and some general observations

can be drawn on the basis of those reports. Greenwood (1988) described a mill scale hardwood/softwood digester conversion from conventional kraft to MCC pulping. After the unit was switched to the MCC mode, previous difficulties with the rate of liquor extraction in the conventional digester were eliminated, and extraction rates well above design levels could be easily maintained.

Data illustrating the potential of the MCC digester for operation at uniform kappa numbers were presented by Kamyr Inc. (Prough, 1990b) and Barnes (1990). The Kamyr data, from Howe Sound Pulp Co. Ltd. in British Columbia, indicate that following a conversion from a conventional kraft digester to an MCC system, the coefficient of variation of the digester kappa numbers decreased from 9.4% to 6.2%. In his report on the Longview MCC digester operation, Mr. Barnes selected two operating charts which show bi-hourly kappa number variations during two different grade runs. The two charts indicated good control of the kappa numbers at average values of approximately 13 for one pulp grade, and 24 for the second grade. The Panel recognizes that these data are of limited scope and do not apply directly to the EMCC system proposed by Alberta-Pacific. Nonetheless, the Panel believes that the potential for good kappa number control in the Kamyr MCC digester is supported by these reports from users of the technology.

Additional information presented by Kamyr Inc. (Prough, 1990a) illustrated that aspen pulp offers superior runnability in the MCC mode, in comparison to other wood species. A plot entitled "Effect of Species on Capacity" demonstrated that at any given chip compaction pressure, the throughput for a specific digester was greater for aspen pulp than for any of the other species tested. This enhanced runnability with aspen was attributed by Mr. Prough to the fact that aspen chip plugs maintain a very open structure (Transcript, p. 612). The Panel understands that the greater permeability of the aspen chip plug may further enhance the improved extraction rates found in a number of MCC digesters (Prough, 1990a).

Finally, Mr. Barnes reported the opinion offered by an MCC digester operator at the Longview Fibre mill (Barnes, 1990). The operator stated that "he had quite a long learning curve with the MCC." However, "now that he has ironed out the wrinkles he prefers the MCC over the conventional digester".

4.1.5 Effects on Downstream Pulp Processing

The EMCC pulp digester is located in the heart of the proposed Alberta-Pacific fibreline. If significant changes in pulp quality result from the substitution of EMCC technology for the original MCC system, such changes could have impacts on one or more of the downstream unit processes. In an attempt to assess downstream impacts, the Panel reviewed material presented to it that dealt with kappa number uniformity, rejects rates and pulp bleachability. The available information on kappa number uniformity was discussed briefly above. Although the data were limited in scope, the Panel notes that they were sufficient to suggest that the MCC system has the capability of producing pulp with highly uniform kappa numbers. The Panel also recognizes that the attainment of uniform pulp quality will be only partly dependent on the use of a particular digester design. Good operator training and modern computer-based process control will also be required to minimize variations in pulp quality from the digester.

The kappa number data reviewed above provide a positive indication of the potential of the MCC-type systems. Conversely, Dr. Berry (PAPRICAN, 1990) reported that pulp non-uniformity has been a problem in MCC digester systems that have been operated in a counter-current mode. Dr. Berry further suggested that these non-uniformity problems may be caused by "uneven counter-current flow which is an integral component of the modified digester system". The Panel sought to clarify the issue of pulp uniformity by examining the material presented that was based on other indicators of pulp quality.

A data set for a one-month operating period during the conversion of an unidentified digester from conventional to MCC cooking was presented by Kamyr Inc. (Submission No. 39). The MCC operating mode resulted in a substantial decrease in the shives content of the feed to the screens. Information submitted by Barnes (1990) indicated that the Longview softwood MCC system operated at very satisfactory rejects levels of between 0.1% and 0.2% over a kappa number range of 12 to 25. Of particular interest is the observation that rejects rates appeared to be lower when lower kappa number pulp was being produced. Lastly, highly anecdotal information was presented by Kamyr (Prough, 1990a) indicating that low rejects rates are a common feature of the five operating MCC systems reviewed.

No data on the bleachability of EMCC pulps were submitted to the Panel. However, information contained in the Mitigative Response suggests that less chemical is required for the bleaching of MCC pulps than for conventional kraft pulps. On behalf of Alberta-Pacific, Mr. D. Herschmiller reported that the Alberta-Pacific hardwood pulp would require a total active chlorine to K number multiple of 0.5 to achieve a brightness of 90.5 CPPA (Transcript, p. 616). This datum was calculated from the single hardwood bleaching trial results submitted by Alberta-Pacific. Greenwood (1988) summarized the bleaching responses of MCC and conventional kraft pulps from two mill scale studies. The hardwood MCC pulps required less chemical to reach a given brightness level. The softwood data also indicate that less chemical was required to bleach MCC pulp to a 90% ISO brightness when compared to a conventional pulp at the same kappa number.

4.1.6 Extent of Operating Experience

Mr. Prough of Kamyr Inc. told the Panel that there are fifteen MCC systems currently in operation at mill scale (Prough, 1990a). Of the fifteen units identified by Kamyr Inc., ten are in North America, including three in Canada. Operating experience with the Kamyr MCC system extends from 1983 to 1990 and MCC digester technology appears to have become a standard for application to greenfield mills and for re-builds of existing mills. Operating experience with EMCC digester technology is more limited. Alberta-Pacific reported in the Mitigative Response that partial EMCC operation has been implemented or planned through white liquor addition to the counter-current zone at Augusta, Georgia; Iggesunds, Sweden and Columbus, Ohio. Dr. Berry summarized PAPRICAN's understanding of the operating experience with EMCC digester systems (Berry, 1990). He reported that hardwood partial EMCC systems have operated for six months, and that the period of softwood EMCC pulping is two months. Dr. Berry also informed the Panel that no mill scale experience with full EMCC pulping (black liquor pre-impregnation) had been identified to date by PAPRICAN.

4.2 Oxygen Delignification

The oxygen delignification stage proposed by Alberta-Pacific in the Mitigative Response is unchanged from that proposed originally in 1989. As submitted by Dr. Sarkanen (Sarkanen,1990) the oxygen delignification stage will only be required to remove approximately 35% of the lignin remaining in the pulp after EMCC digestion. Oxygen delignification systems were originally designed for 50% delignification. However, 30% to 40% delignification is now used routinely in these systems to ameliorate yield and strength loss (Reeve,1989). The Panel accepts Dr. Sarkanen's assertion that the low incoming kappa numbers will permit conservative operation of the oxygen delignification system.

The Panel further accepts that oxygen delignification technology has been in use at mill scale for many years and, as such, can be considered to be proven. Alberta-Pacific has not proposed any substantial deviations from normal design or operating practice for oxygen delignification systems.

4.3 Pulp Bleaching

Three significant changes in the bleach plant have been proposed by Alberta-Pacific in the Mitigative Response. These are:

1) an increase in the size of the $D_{\varnothing}$ tower to provide more retention time to permit 100% chlorine dioxide bleaching,

2) the re-design of the oxygen extraction stage to permit operation at a higher temperature and pressure, plus the addition of a liquid peroxide solution to the oxygen extraction stage, and

3) the installation of a full D_n stage with an associated washer.

No additional chlorine dioxide generation capacity will be required because the modified fibreline design will reduce the total amount of chlorine dioxide required for pulp bleaching.

4.3.1 100% Chlorine Dioxide Substitution

From the perspectives of design, construction and operation, pulp bleaching towers utilizing 100% chlorine dioxide can be considered to be proven technology. It is important to note that the chlorine dioxide is added to the pulp as a dilute solution at a concentration of approximately 10 g/L. Although the use of 100% chlorine dioxide in the $D_{\varnothing}$ stage of a bleached kraft mill is a relatively novel application for the technology, the Panel can see no reason why such a tower should operate differently from the more common applications in the D_1 or D_2 stages. In the brightening stages of kraft bleach plants, 100% chlorine dioxide has been used successfully for many years.

In his submission to the Panel (PAPRICAN, 1990), Dr. Berry indicated that the major drawbacks expected with the "highest levels of substitution are the lowered brightness thresholds for the pulp and the increased chemical cost". Sarkanen (1990) submitted

that "the success of some Scandinavian mills in complete elimination of elemental chlorine from hardwood pulp bleaching is a guarantee for achieving satisfactory brightness". Both submittors acknowledged that the inclusion of a hydrogen peroxide-reinforced E_o stage will be important in the attainment of the target brightness levels, particularly with softwood.

4.3.2 Peroxide Addition to the Pressurized E_o Stage

Hydrogen peroxide is the dominant bleaching chemical used in the chemi-thermomechanical pulping industry. Although not yet in wide use in the kraft pulp sector in North America, it is widely used in Sweden. As proposed by Alberta-Pacific, the equipment required for utilizing peroxide in the E_o stage is relatively simple. First, the upflow tube on the extraction stage must be upgraded to a presssure vessel capable of operation at 2 to 3 bar at temperatures between 85 and 90° C (Alberta-Pacific *et al.*, 1990). Second, the appropriate pumps, valves and metering equipment must be installed for peroxide addition upstream of the upflow tube. One Canadian kraft mill has reported successful operation of an oxygen-peroxide extraction stage for the past sixteen months with a lower pressure upflow tube (Reid *et al.*, 1990). The process conditions in the E_{op} stage are still undergoing optimization, but no operating difficulties were reported by the mill.

PAPRICAN (1990) and Carmichael and Althouse (1986) have shown that peroxide reinforcement of the E_o stage is effective in reducing the CE kappa number (kappa number after E_{op}) relative to that obtained with E and E_o operation. By enhancing the amount of lignin removed in the extraction stage, the bleaching conditions in the $D_{\varnothing}$ and brightening stages can be less aggressive. This will assist with the minimization of chlorinated organic matter formation during chlorine dioxide bleaching and brightening.

4.3.3 Overall Bleach Plant Performance and Chemical Requirements

The Panel received only one piece of experimental evidence (Becker and Holloran, 1990) that would permit it to verify the anticipated performance of the revised bleach plant. This bleaching trial also forms the principal basis upon which the Panel could estimate the chemical requirements of the revised sequence. The trial was performed with aspen collected from the Athabasca area. The wood was chipped and pulped in a laboratory digester under conditions similar to those anticipated in a mill scale EMCC digester system. The EMCC kappa number was 8.9. Following an oxygen delignification stage, the 6.9 kappa pulp was bleached in a $D_{\varnothing}$-E_{op}-D sequence. This is a shortened version of the sequence now proposed by Alberta-Pacific. After bleaching in the short sequence, the final bleached pulp brightness was 90.8 Elrepho. This brightness level slightly exceeds the target of 90.5 indicated in the Mitigative Response. No data on softwood bleaching with this sequence were reviewed by the Panel. The Panel used the chemical application rates described in the aspen bleaching trial to estimate chemical requirements for oxygen delignification and bleaching. To estimate the required amounts of sodium chlorate, a conversion efficiency of 95% was assumed for the chlorine dioxide generator. The estimated chemical requirements for aspen bleaching at an EMCC kappa number of 8.9 are summarized in Table 4.3.1 below. For the estimated sodium chlorate consumption rate of 13.6 kg $NaClO_3$/ADt, the equivalent chlorine dioxide application rate summed over all stages of the bleach plant would be 8.2 kg ClO_2/ADt.

Table 4.3.1

Estimated Chemical Application Rates for Aspen and Softwood Bleaching

Chemical	Chemical Application Rates (kg/ADt) Revised [a] (Aspen)	Panel Estimate (Aspen)	Panel Estimate (Softwood)
Sodium Hydroxide	11.8	7.5	NC*
Magnesium Sulfate	4.5	5	NC
Chlorine Dioxide	15.1**	8.2	15.1
Sulfuric Acid	19.4	21.4	NC
Hydrogen Peroxide	3	3	NC

*NC—not calculated
** Calculated from sodium chlorate consumption.
[a] Alberta-Pacific *et al.* ,1990.

Since no data were available for softwood bleaching, the Panel took a simple approach to estimate the softwood chlorine dioxide application rate. According to PAPRICAN (1990) an average aspen kappa number after oxygen delignification would be 6.5. This value compares well to the unwashed pulp of 6.89 kappa used during the Alberta-Pacific bleaching trial. The corresponding average kappa number for oxygen delignified softwood given by PAPRICAN is 12.0. By assuming the same extent of delignification in the bleach plant for both softwood and hardwood, the ratio of chlorine dioxde used for softwood bleaching to that for hardwood bleaching might be equal to the ratio of the corresponding kappa numbers for oxygen delignified pulps. The application of this ratio (12/6.5) to the chlorine dioxide consumption estimated for hardwood bleaching results in a calculated value of 15.1 kg ClO_2/ADt for softwood bleaching. This value is very approximate and it may be an underestimate if a greater extent of chlorine dioxide delignification is required when bleaching softwood. The same 95% generation efficiency was then used to determine that the sodium chlorate requirement for softwood bleaching would be 25.2 kg $NaClO_3$/ADt.

The chemical requirements estimated by the Panel from the Alberta-Pacific aspen pulping trial differ substantially from those presented in the Mitigative Response (Alberta-Pacific *et al.*, 1990; p. 90). The Panel understands that the consumption rates shown in the Mitigative Response were estimated prior to the execution of the experimental aspen bleaching trial and therefore are not directly related to the effluent quality data summarized by Alberta-Pacific *et al.* in Tables 5.4 and 5.5. This discrepancy, which was the source of a great deal of confusion for reviewers of the Mitigative Response, could have been avoided had the authors given more attention to consistency.

The Panel notes that its estimated chemical application rates are based on the results of a single laboratory bleaching trial, and therefore do not make any allowance for

replication variability or for process scale-up. Nonetheless, the Panel is satisfied that the chemical application rates estimated in Table 4.3.1 more accurately reflect the probable rates for mill scale application of molecular chlorine-free bleaching technology, than those submitted by Alberta-Pacific. Indeed, the chlorine dioxide figure in Table 4.3.1 may overestimate the mill scale requirement for chlorine dioxide, in that the laboratory scale bleaching trial was conducted with a short sequence version of the bleaching process. At mill scale, brightening may be accomplished in two chlorine dioxide stages instead of the one stage used in the laboratory trials (Alberta-Pacific *et al.*, 1990). The additional inter-stage washing and the extra retention time in the full sequence may permit less aggressive bleaching conditions to be used overall. This could provide the dual advantages of reduced yield loss with decreased bleaching chemical application rates and AOX generation.

4.4 Feasibility of the Combined Unit Processes

In its review of the environmental impact of the original mill design, the Review Board expressed concern "that the various processes combined in Alberta-Pacific's calculations have not been previously tested in one combined treatment system. It is thus not known whether the combined treatment will be as efficient as the sum of the various elements." (EIA Review Board, 1990). The "treatment processes" referred to by the Review Board included "oxygen delignification, extended cooking, chlorine dioxide substitution and activated sludge treatment". A number of submittors to the Panel also expressed the same concern for the unproven nature of the combined process train.

The Panel chose to address this matter from two points of view. The most important of these may be the question of whether the individual contributions of each unit process to the minimization of organochlorine generation are additive across the entire fibreline and the wastewater treatment plant. This issue will be dealt with in Section 5. The second question deals with the feasibility of the operation of the combined unit processes. A number of submittors agreed that individually, all of the unit processes could be considered to be "leading edge" but proven technologies. However, there may be a residual concern that, in combination, operational problems could occur that could not be predicted from the mill scale experience to date with the individual processes.

The Panel accepts that each of the unit processes proposed by Alberta-Pacific for mitigation of the discharge of organochlorines has been demonstrated in mill scale operation somewhere in the world. In the cases of oxygen delignification and bleaching tower operation with 100% chlorine dioxide, the available operational history is extensive. The Panel further accepts that in a mill setting the pulping and bleaching processes can operate almost independently. The Panel was told by Mr. Prough (Transcript, p. 140-141) that pulp at various stages of processing can be accumulated in intermediate storage tanks. In some cases, unbleached pulp is actually shipped to a different mill site for bleaching. Mr. Fenner informed the Panel that the degree of operational independence is such that individual unit processes can be operated at different production rates (Transcript, p. 734) by adding to, or drawing from the intermediate storage inventories as required. For a limited period of time it is possible to run one or more of the individual unit processes while other areas of the mill are completely shut down. From this understanding of pulp mill operation, the Panel can see no reason why the individual unit processes should be more difficult to operate in combination than in isolation.

Although the operational interactions of the Alberta-Pacific unit processes may not be significant, this conclusion does not apply to the pulp quality, or to the characteristics of the wastewater generated in the processes. As discussed above, the quality of the pulp at any stage in the fibreline will be dependent on the operation of the upstream processes. Similarly, minimized organochlorine discharge rates will only be achieved through the combined contributions of many of the components of the fibreline.

Several submittors expressed the opinion that the Alberta-Pacific pulp mill design should be assessed at pilot scale before any consideration is given to approving the full scale mill. In Canada, limited pilot scale facilities for developing and demonstrating pulp and paper manufacturing processes are available at research institutions such as PAPRICAN, and a small number of privately-owned industrial research centres. Pilot scale facilities are not widely used by industry for demonstrating mill designs partly because of the problems associated with the handling of materials at a small scale. In continuous manufacturing systems, such as those which process chips or pulp, the occurrence of handling and conveying problems can be inversely related to the scale of operation. At a small scale, it may be very difficult to simulate the chip or pulp transport characteristics required in a mill scale process. For these reasons, pulp and paper mill designers usually prefer to make incremental improvements on existing mill scale technologies, rather than attempting to demonstrate major process changes through pilot scale experimentation.

An illustrative example was reported by Alberta-Pacific *et al.* (1990) in the discussion of the early experience with MCC technology at Aanekoski, Finland. Even at mill scale, problems were encountered with chip plug hanging because the Aanekoski digester was too narrow. These problems were solved at mill scale by gradually evolving wider MCC digester designs to improve runnability. Since larger vessels were needed to solve these problems, it would have been very difficult to develop a solution through experimentation at a smaller pilot scale. Mr. Prough indicated (Transcript, p. 611-612) that continuous flow digester conditions can be modelled with mathematical techniques (Harkonen, 1987), but the testing of these models at pilot scale is only feasible in a batch system in which there is no flow of chips or pulp. In the mill scale design proposed by Alberta-Pacific, all of the processes must operate in a continuous flow mode such that process materials can be continuously conveyed in and out of the unit processes. Continuous operation would be very difficult to simulate properly at a small scale.

The batch mode of testing has already been used by Alberta-Pacific to develop initial data for the mill scale design. The pulping and bleaching trials described by Dr. Becker and Mr. Holloran were conducted using batch-type processing procedures. Further, as discussed previously, the Panel accepts that each of the unit processes proposed by Alberta-Pacific can be considered to be demonstrated technology. Pilot testing of the combined processes in a batch mode would not provide sufficient new information on the operational feasibility of the mill scale continuous process to justify the effort and expenditure required.

4.5 Robustness of the Proposed Design

The objective of the revised pulping and bleaching processes described in the Mitigative Response is to reduce the quantities of organochlorines and conventional pollutants discharged to the Athabasca River. The anticipated reduction in organochlorines is to

be achieved in part by decreasing the kappa numbers of the pulps passed to the bleach plant. If less lignin is removed in the bleach plant, the potential for organochlorine formation should be reduced proportionately. The low kappa number brownstocks anticipated by Alberta-Pacific will also permit the elimination of added molecular chlorine in the bleach plant, in favour of chlorine dioxide and hydrogen peroxide.

The Panel was concerned that the Alberta-Pacific mill design should contain adequate safety factors and contingencies to ensure that the projected kappa numbers can be achieved without difficulty. The extent of delignification achieved in the fibreline should be robust to the many undefined operational problems and disturbances that would otherwise affect delignification. The Panel assessed the robustness of the revised design by reviewing the safety margins available and the contingencies that could be applied to increase delignification in areas of the mill which would not utilize chlorine dioxide.

The Alberta-Pacific revised pulp mill would be designed to achieve EMCC kappa numbers of 10 for hardwood and 23 for softwood. In reviewing the EMCC digester system, Dr. Berry stated that surveys and mill visits by PAPRICAN staff have indicated that minimum kappa numbers of 8 for hardwood and 16 for softwood have been attained at other locations with extended pulping (PAPRICAN, 1990). Sarkanen (1990) submitted that the "targeted kappa range 10 to 12 ought to be possible to reach without extensive charge of white liquor to the counter-current zones of the digester" (ie. MCC may be sufficient). Mr. E. Barnes reported that the Longview MCC digester has operated to kappa 9 on softwood without white liquor addition to the wash zone.

The Alberta-Pacific digester is designed to achieve a more extensive cook with white liquor addition to the wash zone and sufficient heating to allow cooking temperatures to be reached in the counter-current zone (EMCC). If this form of EMCC provides insufficient delignification, selectivity can be improved by increasing the sulfidity at the beginning of the cook by adding black liquor upstream of the impregnation vessel. Dr. Becker told the Panel that the Alberta-Pacific digester could "easily cook down to a 5 or 6 kappa" but that it would designed "for 9, so there is a lot of safety there" (Transcript, p. 642).

The experience to date with basic MCC cooking suggests that the design digester kappa numbers projected by Alberta-Pacific are conservative for both hardwood and softwood. The Panel accepts that the additional capability of operating in an EMCC mode, or EMCC plus black liquor pre-impregnation, greatly increases the robustness of the pulp digester system.

As discussed above, oxygen delignification technology is widely used in the pulp and paper industry. These systems have the capability of achieving greater than 50% lignin removal (Reeve, 1989). The Alberta-Pacific pulp mill design is predicated on the achievement of only 35% delignification in an oxygen delignification system of conventional design. Dr. Becker indicated that if "there were, for example, an upset in the digester, the oxygen stage in this system has enough capacity to lower the kappa number by 50 or 60 percent. If the kappa in the digester went up slightly, you increase the oxygen stage severity to overcome that." (Transcript, p. 642).

Dr. Becker further stated that if "the digester and the oxygen stage system (are) not able to reduce the kappa number going to the first chlorine dioxide stage, ... you could increase the amount of peroxide put into (the E_o stage) on an emergency basis to obtain

your brightness without increasing the AOX in the effluent". In the event that longer term delignification problems are encountered, Mr. Fenner indicated that Alberta-Pacific has examined the possibility of "going with two-stage O_2 systems with a wash stage and perhaps a chelating stage in the middle". Mr. Fenner also told the Panel that some peroxide could be added after the first oxygen stage as well (Transcript, p. 641).

The Panel agrees that these contingency plans are feasible.

4.6 References

Alberta-Pacific Environmental Impact Assessment Review Board (1990). "The Proposed Alberta-Pacific Pulp Mill: Report of the EIA Review Board". February 28, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc., Beak Consultants Ltd. and H.A. Simons Ltd. (1990). "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds". Submission No. 46 to The Alberta-Pacific Scientific Review Panel, September 14, Edmonton, Alberta.

Barnes, E.T. (1990). "Mill Visit Report September 4 and 5, 1990: Longview Fibre Company", Submission No. 34 to The Alberta-Pacific Scientific Review Panel, September 6, Edmonton, Alberta.

Becker, E. and M. Holloran (1990). "Alberta-Pacific Lab Scale Pulping and Bleaching Trial B-1444-1". Submission No. 31 to The Alberta-Pacific Scientific Review Board, September 13, Athabasca, Alberta.

Berry, R. (1990). Overheads for Oral Presentation. Submission No. 26 to The Alberta-Pacific Scientific Review Panel, September 14, Athabasca, Alberta.

Carmichael, D.L. and E.B. Althouse (1986). "Short Sequence Bleaching with Hydrogen Peroxide". Tappi Journal, **69**(11): 90-94.

Casey, J.P. (1983). "Pulp and Paper: Chemistry and Chemical Technology, Volume 1", 3rd Edition, John Wiley and Sons, New York.

Grace, T.M., B. Leopold, E.W. Malcolm and M. J. Kocurek (1989). "Pulp and Paper Manufacture, Volume 5 Alkaline Pulping", 3rd Edition, Joint Textbook Committee of the Paper Industry, Tappi and CPPA, Atlanta, Georgia, USA, and Montreal, Quebec, Canada.

Greenwood, B.F. (1988). "A Review of the Basis for and the Current Status of Modified Continuous Cooking", Presented at the Amer. Inst. of Chem. Eng. National Meeting, November, Washington, D.C.

Harkonen, E.J. (1987). "A Mathematical Model for Two-Phase Flow in a Continuous Digester". Tappi Journal, **70**(12): 122-126.

PAPRICAN (1990). "Assessment of The Improvements Proposed by Alberta-Pacific Forest Industries Inc. to the Wood Pulping and Bleaching Process as They Relate to the Mitigation of the Discharge of Chlorinated Organics Into the Athabasca River", Submission No. 16 to the Alberta-Pacific Scientific Review Board, August 23, Edmonton, Alberta.

Prough, R.J. (1990a). Untitled, Submission No. 40 to the Alberta-Pacific Scientific Review Panel, September 14, Athabasca, Alberta.

Prough, R.J. (1990b). "Kappa Averages: Howe Sound Pulp Co. Ltd.", Submission No. 42 to the Alberta-Pacific Scientific Review Panel, September 14, Athabasca, Alberta.

Reid, D.W., G.G. Billmark and C.J. Sutton (1990). "Peroxide Bleaching Reduces Dioxin Formation in a Generator Limited Mill". Presented at Western Section Meeting, Technical Section, CPPA, May, Jasper, Alberta.

Reeve, D.W. (1989). "Delignification Process Variables" in T.M. Grace, B. Leopold, E.W. Malcolm, and M.J. Kocurek eds., Pulp and Paper Manufacture: Volume 5 Alkaline Pulping, 3rd Edition, Joint Textbook Committee of the Paper Industry, Tappi and CPPA, Atlanta, Georgia, USA and Montreal, Quebec, Canada, p. 459.

Sarkanen, K.V. (1990). "Assessment of the Mitigative Response to Concerns Regarding Chlorinated Organic Compounds. A Process Optimization Proposal by Alberta-Pacific Forest Industries Inc.", Submission No. 27 to Alberta-Pacific Scientific Review Panel, September 12, Athabasca, Alberta.

Whitley, D.L., S.R. Zierdt and D.J. Lebel (1990). "Mill Experiences with Conversion of a Kamyr Digester to Modified Continuous Cooking". Tappi Journal, **73**(1): 103-108.

Section 5—Expected Effluent Characteristics

To make an assessment of the expected effluent characteristics, it was essential to explore the following:

- the nature and abundance of chlorinated organic compounds in pulp bleaching effluents,
- the chemistry of their formation,
- the quantities formed in the revised fibreline mill,
- the analytical chemistry associated with their detection in pulping effluents, and
- the removal and fate of the chlorinated organic compounds in the wastewater treatment plant.

This section of the report deals with these subjects as they relate to the effluent from the revised fibreline mill. Conclusions and recommendations are made regarding Alberta-Pacific's claims that the proposal mitigates the discharge of chlorinated organic materials.

5.1 The Nature and Abundance of Chlorinated Organic Compounds in Pulp Bleaching Effluents

Bleached kraft mill effluent is a complex mixture of organic compounds and inorganic ions that arises from the processes carried out to remove lignin from the wood during the production of bleached pulp. The portion of the organic compounds that are most difficult to treat, and problematic in the environment, includes organic compounds that have chlorine incorporated in their structures as a result of the bleaching processes.

It is this mixture of compounds that forms the chlorinated organic material discharges referred to in the Ministerial Order. The nature of the mixture is very complex. It depends on the pulping and bleaching processes used, the wood species pulped, and on the wastewater treatment processes, if any, employed before effluent discharge. Because of the complexity of the mixture and its variability, chemical characterization is very difficult. It has therefore become common practice to use the group parameter known as "Adsorbable Organic Halogen" as a measure of the concentration of all organically-bound chlorine in effluents. This is commonly called AOX and is usuall reported as mg/L of chlorine in the effluent. In order to compare AOX production rates, the effluent AOX concentration is multiplied by the effluent flow rate for a unit of pulp production, and the result is expressed in terms of mass of organically-bound chlorine per unit of pulp production, usually kg AOX/ADt pulp.

Table 5.1.1 describes the nature and abundance of various categories of chlorinated compounds in typical bleached kraft pulp mill effluents. It was originally presented by Dr. Reeve during his introductory comments at the Athabasca Workshop (Reeve, 1990a).

Table 5.1.1

Chlorinated Organic Compounds
in Bleached Kraft Mill Effluents [a]

	Varieties	Amounts
Chlorinated Acids	40	up to 500 g/t
Chlorinated Phenolics	40	up to 100 g/t
Chlorinated Adehydes, Ketones & Lactones	45	500 g/t
Chlorinated Hydrocarbons	45	unknown traces
Chlorinated Others	20	unknown traces
Chlorinated High Molecular Weight Matter	not applicable	up to 4 kg/t as Cl
Chlorinated Dioxins & Furans	30	10^{-4} g/t

(a) From Reeve (1990a)

A minute fraction, about one billionth of the total AOX in conventional bleached kraft mill effluents, consists of chlorinated dibenzo-para-dioxins and dibenzofurans. These groups of chlorinated organic compounds, commonly referred to as "dioxins and furans", include certain compounds that have been shown to be highly toxic in laboratory experiments using animals. These are mainly the tetrachlorinated dioxins and furans with chlorine substituents at the 2, 3, 7 and 8 positions. They are commonly referred to as 2, 3, 7, 8-tetrachlorodibenzodioxins/furans or 2, 3, 7, 8-TCDD/F. Because bleached kraft mills have been shown (Anderson *et al.*, 1990) to contain 2, 3, 7, 8-TCDD/F, among other dioxins and furans, considerable effort has been devoted to understanding the mechanisms of formation and the options for control of these substances in pulping effluents.

Other constituents of environmental concern in the treated effluent are chlorinated phenolic compounds that arise during the degradation of lignin in the bleaching processes.

The Panel has considered both of these goups of contaminants, in addition to the AOX, in defining the expected effluent characteristics from the revised fibreline mill.

5.2 The Mechanism of Formation of Chlorinated Organic Compounds in Pulp Mill Effluents

Chlorinated organic compounds are formed during the bleaching of pulp by the attack of chlorine on lignin and its breakdown products and, to a lesser extent, wood extractives. The reactions were discussed by Dr. Sarkanen (Transcript, p. 98-100) and Dr. Armour (Transcript, p. 195-204). Both contended that among the chlorine containing species present in bleaching reactions only molecular chlorine is capable of chlorinating the phenyl groups and the side chains of the lignin. This contention is well supported in the literature and is generally accepted in mechanistic organic chemistry. Chlorine dioxide itself is not capable of chlorinating organic compounds.

In practice, complete replacement of molecular chlorine by chlorine dioxide in the bleach plant is not possible. In Dr. Plambeck's presentation to the Panel, he pointed out (Transcript, p. 321) that some molecular chlorine is formed during the bleaching processes with chlorine dioxide. Dr. Reeve also stated: "It (the chlorine dioxide generator itself) produces a very small amount of molecular chlorine.....Molecular chlorine is present in the solution as it passes to the bleach plant, and will represent something like 1% of the oxidizing power of the solution. So you could think of the chlorine dioxide as being 99% pure." (Transcript, p. 36).

Investigations by Germgard and Larsson (1983) and Earl and Reeve (1989) have demonstrated that about 10% of the chlorine (whatever its chemical form) applied during bleaching can be found in the AOX produced. In one Canadian mill this has been found to be an overestimate of the actual AOX production (Cook, 1988). Nevertheless, it is clear that 1% contamination of the chlorine dioxide does not represent sufficient molecular chlorine to produce the AOX levels that have been measured. Therefore, molecular chlorine formed *in situ* during the bleaching reactions must account for the majority of AOX formed. Kinetic and mechanistic studies of the bleaching reactions have been reported by Wartiovaara (1982), Hong and Rapson (1968), Germgard (1982), Teder and Tormund (1977) and Kolar *et al.* (1983). From these studies it is apparent that hypochlorous acid formed in the bleaching reactions is the source of the molecular chlorine.

The molecular chlorine present in a bleaching tower is subject to several competing demands. Chlorine is consumed by the bleaching reactions, the chlorination of phenolic compounds that are produced by the action of chlorine dioxide on lignin, the addition of chlorine to unsaturated aliphatic compounds produced similarly, and the chlorination of dioxin and/or furan precursors. Unchlorinated furan precursors have been identified by Voss *et al.* (1988) in unbleached pulp and are believed to be the source of 2, 3, 7, 8-TCDF formed during bleaching.

The reactions of chlorine with lignin are dominant due to the high reaction rates and the relative abundance of lignin. These reactions also produce phenolic and aliphatic compounds that in turn compete for the available molecular chlorine. The chlorinations of phenolic compounds and the dioxin precursors are electrophilic substitution reactions that become slower and more difficult as the degree of substitution increases. That is, the rates of reaction of each successive substitution of chlorine decrease by about two orders of magnitude compared to the preceeding step (Sullivans, 1980). The dioxin precursors are believed not to be replenished in the same fashion as the phenolic

compounds and as their concentrations drop, the precursors compete less successfully for the available molecular chlorine.

It follows that strategies that remove molecular chlorine from the bleaching reactions can decrease the production of AOX, and reduce the likelihood of multiple chlorinations of the phenolic compounds and dioxin precursors. Such strategies include increasing the degree of chlorine dioxide substitution and reducing the active chlorine multiple, a measure of the total oxidizing chemical applied to the pulp during the first stage of bleaching.

In his submission to the Panel, Dr. Berry indicated that studies at PAPRICAN have focussed on determining the relationship between the production of chlorophenols and 2, 3, 7, 8-TCDD/F, the active chlorine multiple used and the degree of chlorine dioxide substitution (Berry, 1990). Figure 5.2.1 presents an example of this relationship. It defines a zone of bleach plant operation in which 2, 3, 7, 8-TCDD/F are produced, because of the excess of molecular chlorine in the bleaching reactors. It also demonstrates that there exists a set of bleaching conditions where the production of 2, 3, 7, 8-TCDD/F is reduced to "background levels".

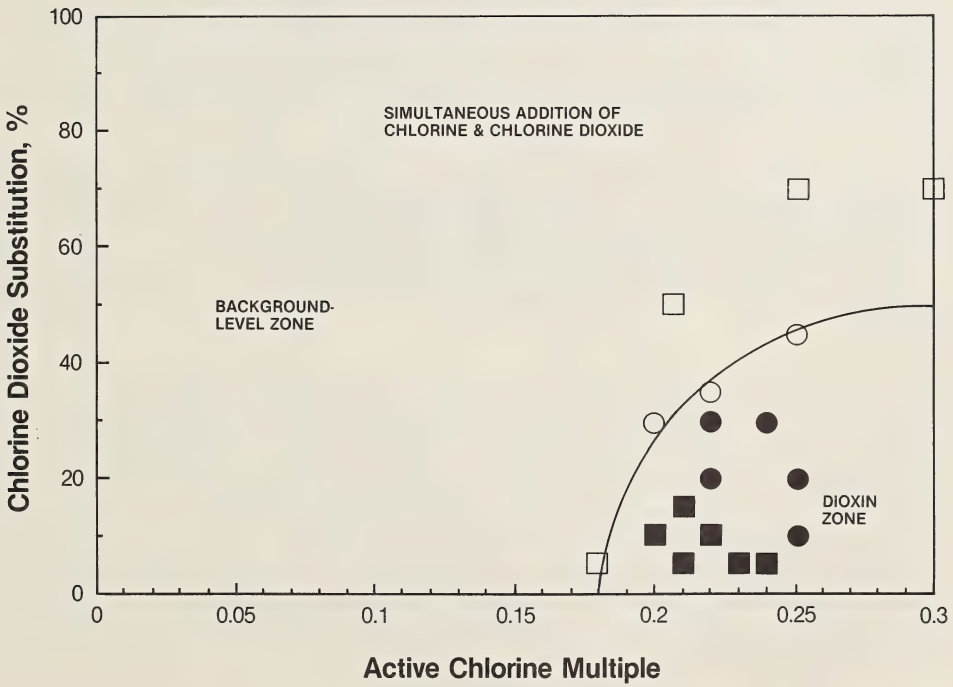


Figure 5.2.1 Relationship Between Appearance of 2, 3, 7, 8-TCDD/F on Pulp, Active Chlorine Multiple and Chlorine Dioxide Substitution. Results at background levels of 2, 3, 7, 8-TCDD/F represented by ❑ for mill scale, ○ for lab scale, and above background levels represented by ■ for mill scale and ● for lab scale (Berry, 1990).

Following Dr. Berry's presentation, data were presented from two kraft mills in British Columbia. Although these mills apparently were operating outside the dioxin production zone, they were found to have measurable 2, 3, 7, 8-TCDD/F in their effluents (Transcript, p. 170). At these levels, the mills would be in contravention of the proposed federal pulp and paper regulations which call for non-detectable levels of 2, 3, 7, 8-TCDD/F in effluents. It appears that operation outside of the PAPRICAN demarcation line will not guarantee a 2, 3, 7, 8-TCDD/F-free effluent. However, based on the discussion of chlorination mechanisms presented previously, the Panel accepts that operation with 100% chlorine dioxide greatly reduces the probability of 2, 3, 7, 8-TCDD/F formation in the bleach plant. None of the British Columbia examples contradicted the hypothesis that dioxins would not be produced at that substitution level.

5.3 The Quantities of AOX Produced in the Revised Fibreline Mill

The Mitigative Response contains some projected discharges of chlorinated organic matter from the proposed plant (Alberta-Pacific *et al.*, 1990; p. 110). The discharge of AOX from the bleach plant was given as 0.43 kg/ADt. When the validity of this figure came under discussion, it became apparent that the 0.43 figure had been calculated on an oven dry tonne basis and should be revised to 0.39 kg/ADt. It was also noted that this figure had been derived from a single analysis of a single laboratory bleaching trial (Becker and Holloran, 1990). On its own, as was correctly pointed out by Dr. Plambeck, such a figure was not credible because its reproducibility is not proven and no estimate of variance is possible.

It became necessary, therefore, for the Panel to consider this value in terms of its consistency with other data. Further AOX discharge values exist from experimentation at 100% chlorine dioxide substitution—notably those presented by Dr. Berry from PAPRICAN (which included a mill trial), a value published in a recent conference proceedings (Suess *et al.*, 1990), and from recent research by Dr. Reeve (Reeve, 1990b).

One observation from Dr. Berry's presentation was that, at a fixed active chlorine multiple of 0.2, the AOX production was proportional to the unbleached kappa number at 10% chlorine dioxide substitution. The Panel plotted the AOX data for 100% substitution at an active chlorine multiple of 0.20 to produce Figure 5.3.1. Most of the data points are of less than ideal reliability individually. While PAPRICAN replicated their data by approximate confirmation, the data points contain no estimate of variance. The literature data are not accompanied by full disclosure of variance. Nevertheless, they show a reasonably linear trend, shown with 95% confidence intervals for the regression line in Figure 5.3.1. The single value provided by Alberta-Pacific is consistent with other data presently available.

The upper confidence limit of Figure 5.3.1 suggests that, at a hardwood kappa number of 6.5, the AOX in a bleach plant effluent may be expected to be below 0.45 kg/ADt with 95% confidence. The appropriate figure for a softwood pulp entering the bleach plant at kappa 14 is 0.70 kg/ADt. The confidence intervals are relatively large because few verifiable data were available to the Panel. However, the Panel is aware that other bleaching trial data have become available since the Mitigative Response was submitted. Also, in the normal course of process development, further bleaching trials will

probably be carried out. All such additional data can be used to verify the Panel's estimates. The Panel's analysis depends on the assumption that effluent AOX values for continuous mill operations may be simulated accurately by bench scale batch bleaching trials. The predicted AOX values of interest are at the lower limit of the kappa number data range. At best, they represent the long term average upper limits of the AOX discharge.

Figure 5.3.1 also suggests that the species of the wood pulp reaching the bleach plant is immaterial to AOX generation. The difference between species is of importance only in the pre-bleach stages, due to the relationship between species and kappa number achievable. Once in the bleach plant, a hardwood or softwood of the same kappa number appears to yield the same AOX discharge.

The flexibility and robustness of the bleaching sequence proposed suggests that if required, the AOX values calculated could be reduced further. A further 20% reduction might be obtained by the operation of the first $D_{ø}$ stage at an active chlorine multiple 20% below 0.20 (i.e. 0.16). Dr. Berry provided Figure 5.3.2, which shows that a larger kappa decrease per unit of active chlorine multiple can be obtained at a lower active chlorine multiple (i.e. 0.14 vs 0.20), by converting the E_o to an E_{op} stage. The resulting small loss

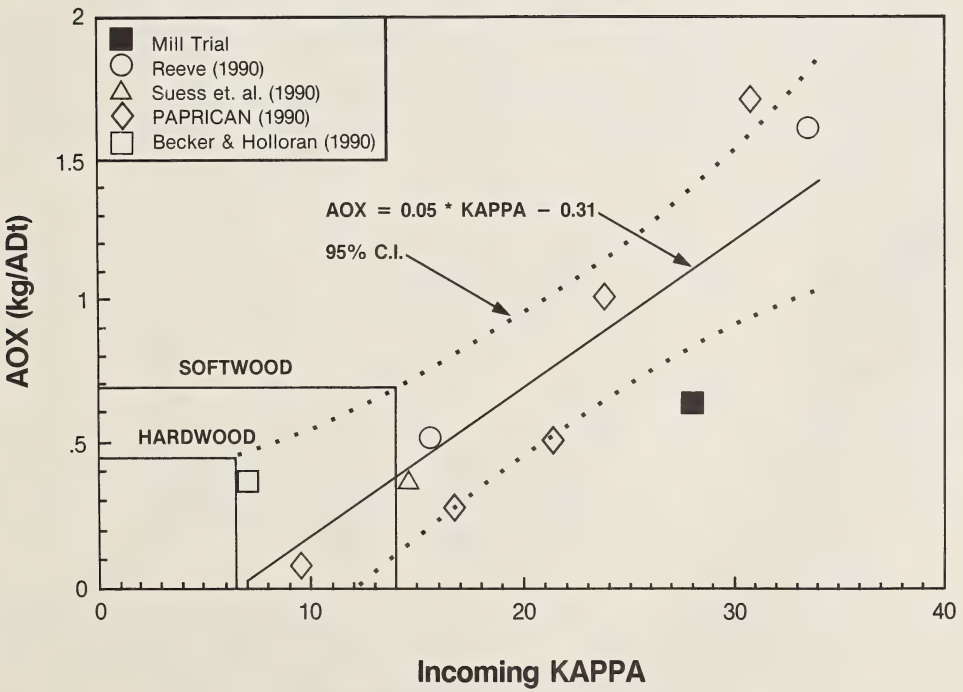


Figure 5.3.1 Relationship Between AOX Generation and Kappa Number of Pulp Entering The Bleach Plant.

of E_{op} stage delignification could then be compensated for by adjusting the chlorine dioxide charge in the later stages. This idea has been successfully applied in an operating mill (Reid *et al.*, 1990).

Evidence of a speciation change of AOX was shown by Berry (1990). Bleaching trials at successive chlorine dioxide substitution levels from 0 to 90% showed that production of all chlorophenolics except the chlorovanillins decreased by 1-2 orders of magnitude, while the AOX decreased by a factor of approximately 5. The chlorovanillin production reached a maximum at 70% substitution. Between 0 and 70% substitution there was a shift towards dichlorinated phenolic compounds from the more highly chlorinated tri- and tetra-chloro catechols and guaiacols.

Figure 5.4 of the Mitigative Response utilizes PAPRICAN data for softwood bleaching between 0 and 90% chlorine dioxide substitution, and combines them with the effluent analysis of Alberta-Pacific's own single hardwood bleaching trial at 100% chlorine dioxide substitution. The data are presented in a manner that suggests a serious discontinuity between the data sets. Also no data for softwood bleaching chlorophenolic compound production at 100% chlorine dioxide substitution was evident in Alberta-Pacific's submission. In view of this apparent discontinuity, and the absence of an important datum, the Panel examined these data in some detail in order to test their validity and to estimate the missing value.

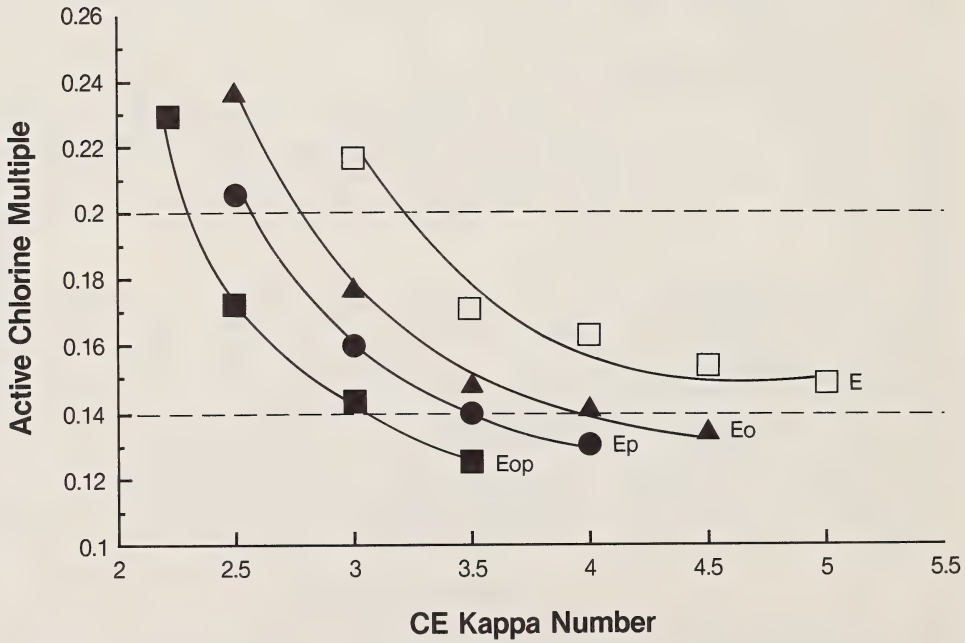


Figure 5.3.2 Relationship Between Active Chlorine Multiple and Alkaline Extraction Stage Kappa Number for Various Extraction Stage Conditions (Berry, 1990).

First, the Alberta-Pacific data suggested a significant improvement in detection limits over the PAPRICAN analyses. The Panel therefore reviewed the analytical technique used in the Alberta-Pacific trials and is satisfied that this technique is appropriate and that it has indeed achieved a substantial lowering of the detection limit. Second, the PAPRICAN data were converted from a chlorophenolic concentration basis to a chlorophenolic-chlorine basis, and plotted against percent chlorine dioxide substitution (Figure 5.3.3). An extrapolation of the regression line to 100% chlorine dioxide substitution meets the value from the Alberta-Pacific trial within normal experimental error. The Panel is satisfied that the softwood bleaching chlorophenolic compound production value is less than 10 g/ADt or 2.0 g of chlorophenolic -Cl/ADt. These values represent the 95% upper confidence limit at 100% chlorine dioxide substitution from Figure 5.3.3. In the absence of other data for hardwood, the Panel reluctantly accepts Alberta-Pacific's estimate of the hardwood chlorophenolics discharge rate of 18.5 mg/ADt.

Figure 5.3.3 might be interpreted to suggest that dissolved phenolic material is not formed to a signficant extent in bleaching with 100% chlorine dioxide, and therefore is not available to react with molecular chlorine. An alternative explanation for the lower chlorophenolic material production is that other materials formed during 100% chlorine dioxide bleaching scavenge molecular chlorine too rapidly for electrophilic substitution reactions to compete.

The Panel has also reviewed the information regarding dioxin and furan production in the revised fibreline mill. The operating conditions of 100% chlorine dioxide substitution and active chlorine multiple of 0.20 are indeed outside the "dioxin production" zone (Figure 5.2.1). Further confirmation of the work of Berry *et al.* (1988) in this area has been provided by a report of a monitoring survey of Scandinavian mills (Rappe *et al.*,

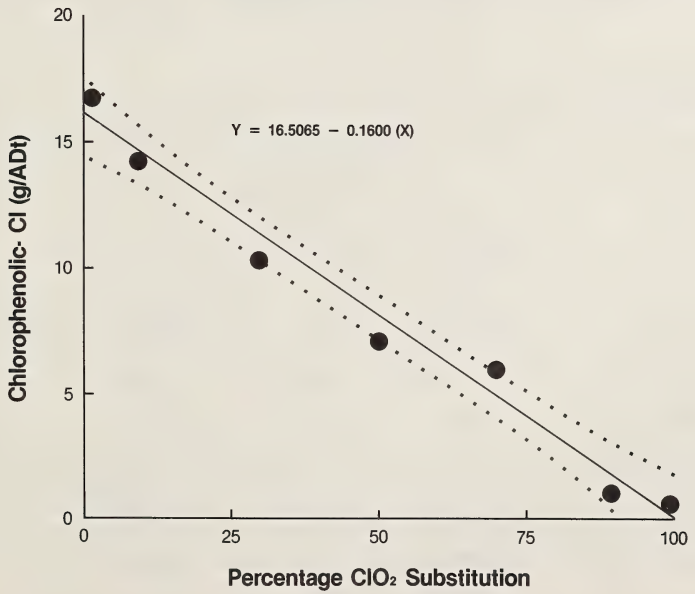


Figure 5.3.3 Relationship Between Softwood Pulp Bleaching Chlorophenolic—Cl Production and Percent ClO_2 Substitution at an Active Chlorine Multiple of 0.2 with 95% Confidence Limits (Derived from Berry, 1990).

1989). This survey indicated that the chlorinated dioxin/furan profile for a bleached kraft mill employing 100% chlorine dioxide substitution should be essentially the same as that of a TMP mill, and both are substantially lower than that from a mill utilizing recycled paper. Tables 5.3.1 and 5.3.2 summarizing this work are shown below.

Table 5.3.1

Dioxins and Furans in Pulps [a]

Contaminant	Kraft Pulp Hardwood 70% ClO_2 (ppt)[b]	Kraft Pulp Softwood 70% ClO_2 (ppt)	TMP Pulp (ppt)	Recycled Pulp (ppt)	Recycled Pulp (ppt)
2, 3, 7, 8-TCDF	0.3	0.4	ND (0.6)	3.6	7.9
2, 3, 7, 8-TCDD	ND (0.5)	ND (0.4)	ND (1.1)	0.3	0.2
Total other CDF	1.5	ND (0.4)	644	711	233
Total other CDD	6.9	1.0	15	308	420

Note: ND = not detected, with the detection limit in parentheses.

(a) From Rappe *et al.*, 1990.
(b) Parts per trillion.

Table 5.3.2

Dioxins and Furans in Pulp Effluents [a]

Contaminant	Kraft Mill Effluent 85% ClO_2 Bleaching (ppq) [b]	TMP Mill Effluent (ppq)
2, 3, 7, 8-TCDF	ND (26)	1.2
2, 3, 7, 8-TCDD	ND (3.5)	ND (1.3)
Total other CDF	1.4	8038
Total other CDD	3057	110

Note: ND = not detected, with the detection limit in parentheses.
(a) From Rappe *et al.*, 1990. Detected amounts only. Detection limits vary widely between samples and congeners.
(b) Parts per quadrillion.

5.4 The Analysis of Chlorinated Organic Compounds in Pulping Effluents

The group parameter AOX is used as a measure of all of the compounds containing organically bound chlorine in water and wastewater. The principle of the analytical technique was discussed by Dr. Reeve (Transcript, p. 28). The method is an adaptation of the standard method used to measure total chlorinated organic compounds in drinking water. Studies have been carried out to test the robustness of the methods (Fraser and Reeve, 1990). They demonstrated that "It is evident that the four most commonly used methods for the determination of AOX in pulp mill effluents show good agreement. The results generated by any one of these are therefore analytically meaningful".

The Panel is satisfied that the AOX test utilized by Alberta-Pacific and its consultants produced reliable data and that the results presented were well above the method detection limit.

Chlorophenolic compounds constitute only a small fraction of the AOX. In effluents they are often present at very low concentrations that challenge the skills of organic analytical chemists. The analytical technique employed involves the extraction of the chlorophenolic compounds from the effluent sample into an organic solvent, several concentration and purification steps (often termed clean-up) and the measurement of each chlorophenolic compound in the mixture by gas chromatography coupled with mass spectrometry. The process is long, complex and fraught with opportunities for error. The method attempts to deal with these difficulties by the use of added standard known chlorinated compounds and assumes the correctness of the result if the correctness of the known standard is demonstrated.

In the case of the chlorophenolic compound analytical data supplied by Alberta-Pacific to support claims for very low chlorophenol production rates, the values obtained from Dr. Becker's single pulp bleaching trial (Becker and Holloran, 1990) are very close to the detection limits. These detection limits (25-50 ng/L) are also lower than those usually reported as pulp mill effluent chlorophenolic detection limits (50-100 ng/L).

The Panel has examined the method employed for these measurements and notes that good standard recovery values were obtained. Therefore, the data from that one bleaching trial sample have credibility. However, the absence of analyses from replicate bleaching trials creates doubt regarding the variability in the very low production rate of chlorinated phenolic compounds estimated by Becker and Holloran (1990).

The analytical method employed for dioxins and furans is similar to that employed for chlorophenolic compounds, except that detection limits must be further reduced, (0.003 - 0.017 ng/L for effluents and 0.1 - 4.9 ng/kg for pulps; Anderson *et al.*, 1990). The Panel has not examined the reliability of the dioxin/furan data supplied to it, but is satisfied that it is consistent with the present state of knowledge and is credible.

5.5 Effluent Treatment

5.5.1 Introduction

Although the revised fibreline will result in a lower waste load to be treated, Alberta-Pacific proposes to utilize the wastewater treatment plant design considered for the original fibreline. The pre-design report by Stanley Associates Engineering Ltd., (1989) originally submitted to the Review Board, has been partially revised to reflect lower input AOX values and correspondingly lower effluent AOX values. However, other changes including BOD_5 loading and daily flow rate of wastewater referred to in the Mitigative Response have not been included in the partially revised pre-design report. This should result in a conservative plant design which offers additional opportunity for reduction of the mass discharges from the mill.

5.5.2 Wastewater Treatment Plant Description

Alberta-Pacific proposes to utilize a standard extended aeration activated sludge wastewater treatment plant. Primary and waste activated sludges would be disposed of by dewatering and burning in the mill hog fuel boiler. The biologically treated effluent would be discharged into the Athabasca River by means of a submerged diffuser. The best description of the plant may be found in the pre-design report submitted to the EIA Review Board (Filed Document #L3) and in an upgraded version supplied to the Panel on August 22, 1990 (Stanley Associates, 1989). While the basic concept remains unchanged, the process design is clearly evolving with respect to flow and materials balance. As noted previously (Section 3.3) some design inconsistencies were apparent. These inconsistencies make the design evaluation difficult and therefore the Panel has chosen to assume the conservative figures presented in the pre-design report of November 1989, as revised in July 1990.

5.5.3 Evaluation of Wastewater Treatment Plant Design

5.5.3.1 Primary Clarification

A single 52 m diameter clarifier is proposed. The design overflow rate is 32.2 $m^3/d/m^2$. This is considerably greater than the recommended value of 24.4 $m^3/d/m^2$ (Alberta Environment, 1989) and will almost certainly lead to solids carryover at peak flows. This may not greatly impact the downstream processing because of the presence of the equalization basin. Consistent primary clarification will prevent loss of equalization capacity due to solids build-up and resulting operating problems associated with solids clean-out of the equalization basin. The solution would be to double the number of primary clarifiers.

5.5.3.2 Emergency Spill Pond

The emergency spill pond is adequately sized. However, partitioning the pond and providing for capture of acid and alkaline spills would allow for more operating flexibility. The operating strategy for the wastewater

treatment plant should include minimizing spill pond contents, in order to allow for capacity to meet all mill contingencies. The construction is referred to as a lined earthen pond. Since the spill pond is likely to contain the most concentrated wastewaters, it may be preferable to utilize a double liner.

5.5.3.3 Equalization and Cooling Pond

This pond will not provide hydraulic equalization to any extent because of its gravity operation. However, in this mill, the peak to average flow ratio is predicted to be 1.2:1, therefore, hydraulic equalization is not critical to the operation of downstream processes. The load (BOD_5) equalization is much more important and the back-mixed configuration and mixing with surface aerators (6) and mixers (6) are adequate to accomplish this during mill operations on either hardwood or softwood. Information was not available to indicate how the wastewater treatment plant might respond during the transition period between wood furnishes. The Panel recognizes that as the wastewater treatment plant control room will be linked to the mill control room, treatment plant operators will have current information on mill changes. This will allow for the judicious use of the spill ponds during the transition if wastewater produced then creates treatment plant upsets. Space should be allowed in the layout of the wastewater treatment plant to provide for additional storage and equalization capacity if the spill pond proves inadequate.

5.5.3.4 The Cooling Tower

The conventional cross flow cooling tower proposed should prove adequate.

5.5.3.5 The Chemical Feed Systems

These have been designed to provide a BOD_5:N:P ratio of 100:5:1 at 25 kg BOD_5/ADt, which will prove sufficient to achieve the treatment goals.

5.5.3.6 Activated Sludge System

The volume under aeration would be approximately 103,000 m^3. At the proposed BOD_5 loading and design mixed liquor suspended solids (1000 - 3000 mg/L) the food to microorganism ratio (F/M) is 0.48 - 0.16 d^{-1}. At the lower BOD_5 loading (16 kg/ADt) the F/M range is 0.3 - 0.1 d^{-1}. The former range is beyond that normally associated with "extended aeration" activated sludge plants, while the latter range is probably adequate to achieve the 94% BOD_5 removal required. It is suggested that the plant design ensure that the aeration capacity provides 1.2 - 1.5 kg O_2/kg BOD_5 removed. The surface aerators may be limited with regard to full-depth mixing and aeration capacity (Alberta Environment, 1989). Consideration should be given to increasing the number of aerators and reducing the basin depth (therefore increasing the surface area).

5.5.3.7 Secondary Clarification

Since the activated sludge treatment process depends on the recycling of sludge, redundancy in the pumping system is essential. The Panel is concerned regarding the operability of the plant at an SRT of 25 days, based on the observation by Rempel *et al.* (1990) that, "Low and high SRTs appear to result in higher TSS levels in the effluent". Provision should be made for additional secondary clarification capacity to counteract poor settling characteristics in the secondary sludge. The design diameter is slightly on the large side, 52 m compared with 50 m recommended maximum (Alberta Environment, 1989).

5.5.3.8 Sludge Thickening and Dewatering

These systems are adequately sized to deal with the waste sludge load.

5.5.3.9 Overall Comments

With the exception of the primary and secondary clarifier overflow rates and the uncertainty of the liner design, the proposed plant design is adequate to carry out the required functions. Allowances must be made to conserve or add heat during mill shut-downs in winter to prevent excessive cooling and freezing.

The Panel notes that Mr. Fenner advised that there are further treatment options that could be applied in the event that adequate removal efficiencies are not achieved (Transcript, p. 669). He also stated that the option of last resort was to shut the mill down (Transcript, p. 671).

5.5.4 Effluent Treatment Plant Performance

The performance expectations for the wastewater treatment plant with regard to BOD_5 and TSS reductions are 94% and 88% respectively (Stanley Associates, 1989). These values are well within the capability of activated sludge treatment technology and the Panel agrees that these treatment goals could be met by an optimized extended aeration activated sludge plant.

The question of AOX removal performance in activated sludge plants is more problematic. Alberta-Pacific expects 45% removal, meaning that the AOX load of 0.50 kg/ADt (hardwood plus softwood weighted average) leaving the bleach plant would be discharged from the wastewater treatment plant at 0.55 X 0.50 = 0.28 kg/ADt. On behalf of Alberta-Pacific, Dr. Pertti Hynninen (Transcript, p. 589) suggested that in order to achieve this, the plant would be operated at a solids retention time (SRT) of 25 days, citing the recent research of Rempel *et al.* (1990). McCubbin (1990), on the other hand, doubted that 45% can be achieved and suggested that 30% is a more appropriate value.

Literature reports on this issue are sparse. The one reference, often cited to support the contention that activated sludge technology is superior to aerated stabilization basins in AOX removal, claims reductions of up to 65% for hardwood pulping and bleaching effluent in a modern Finnish mill (Gergov *et al.*, 1988). The data presented in that report are compared to the proposed Alberta-Pacific mill data in Table 5.5.1. Another report

of mill scale AOX removal in Finland indicated that extended aeration activated sludge technology removed 39% of the influent AOX (Skogman, 1989).

Table 5.5.1
Comparison of Alberta-Pacific Mill and a Modern Finnish Mill

Parameter	Proposed By Alberta-Pacific [a]		Reported From Finnish Mill [b]	
	H/W [c]	S/W	H/W	S/W
Production (ADt/d)	1500	1250	1260	1150
Kappa Number				
• After digestion	10	23	14 - 19	21 - 29
• After O_2 delignification	6.5	14	No O_2 Delignification	
• After first extraction	3.3	2.2	3.2	5.4
Brightness (% ISO)	90	90	90.7	90.0
Chlorine Dioxide substitution (%)	100	100	66	19
Effluent produced (m^3/ADt)	40	48	36.6	35.7
Activated Sludge Plant Retention time (h)	24	24	12	12
Excess Sludge m^3/ADt	2.3	2.3	2.5	2.3
Solids Retention Time [d]	25 [d]	25 [d]	7 - 9	7.9
BOD Reduction (%)	94	94	94	93
AOX Production (kg/ADt)	0.39 [a]	1.1 [a]	1.7	4.8
AOX Discharged (kg/ADt)	0.21 [a]	0.50 [e]	0.6	2.1
AOX Removal (%)	45	45	65	56

Notes: (a) Taken from Alberta-Pacific's documents and presentation
(b) Taken from Gergov *et al.* (1988)
(c) H/W = hardwood; S/W = softwood
(d) Transcript, p. 589
(e) Transcript, p. 567

Two North American mills treating AOX in biological systems have demonstrated that low AOX discharges are achievable. The E.B. Eddy Forest Products Ltd. mill at Espanola, during operation with oxygen delignification, 10% chlorine dioxide substitution and extended aeration effluent treatment (47% AOX removal) in mixed softwood and hardwood pulping, discharged 1.28 kg/ADt (Cook, 1988). Dr. Berry reported (Berry, 1990) that a mill utilizing 100% chlorine dioxide substitution and extensive secondary (biological) treatment (but no extended delignification or oxygen delignification) discharged 0.3 kg/ADt on hardwood and 0.5 kg/ADt on softwood. These results were obtained for one week in every month, presumably due to chlorine dioxide generator capacity limitations.

The most complete information available to the Panel on AOX removal in activated sludge is a report of pilot studies by Rempel *et al.* (1990). The performance for AOX removal was related to SRT. At the 25 day SRT, the AOX removal was 44% (95% confidence interval 37 - 50%). At lower SRT values (5 - 10 days) the removal efficiency

decreased to 15 - 30%. Unfortunately, the level of AOX production in the mill and the nature of the furnish were not reported, so strict comparison to the Alberta-Pacific revised fibreline mill is difficult.

The Panel concludes that in the absence of firm data on the removal efficiency of AOX from the revised fibreline mill, an assumed range of 30 - 50% efficiency is reasonable. This range is assumed to include any AOX removal associated with neutralization of the bleach plant effluents. Therefore, an untreated Alberta-Pacific softwood effluent containing up to 0.7 kg AOX/ADt would be reduced to between 0.35 and 0.49 kg/ADt. The comparable figures for hardwood would be 0.45 kg AOX/ADt for the untreated effluent and 0.22 and 0.32 kg AOX/ADt for the treated effluent. The long term hardwood plus softwood weighted average figures would be 0.50 kg AOX/ADt for untreated effluent, and 0.25 to 0.35 kg AOX/ADt for treated effluent. The effects of AOX speciation changes on the AOX removal efficiency are not known at present, but this should not materially affect these estimates.

Although chlorophenolic compounds form only a minor portion of the AOX content of bleached kraft mill effluent, their importance as environmental contaminants is well recognized (for example, Voss *et al.*, 1981). The Mitigative Response makes reference to unpublished results of Fleming *et al.* on the removal efficiencies of chlorinated phenolic compounds (Table 5.6 in Mitigative Response). The removal efficiencies are shown therein to range from 0 to 85% depending upon the speciation, with the chlorocatechols being the most difficult to remove.

Gergov *et al.* (1988) reported the results of mill scale investigations for both hardwood and softwood pulping and for activated sludge and aerated stabilization basin treatments. They reported removal efficiencies in the range of 76 to 95% for chlorophenolic compounds originating from the bleaching of pine and birch pulps with up to 66% chlorine dioxide substitution. Heimburger *et al.* (1988) reported that chlorophenolic compounds produced as a result of pulping with modified cooking and bleaching with $O(D_c)(E_o)D$ on softwood are reduced during biological treatment by only 14%, to 6 g/ADt. Details of the wastewater treatment processes applied were not reported. Leuenberger *et al.* (1985) reported that effluents from a bleached sulphite mill containing 88 µg/l chlorinated phenols were reduced by 30%, to 62 µg/l. The effluent treatment plant in this case was a two stage activated sludge plant with a 12 hour hydraulic residence time. Skogman (1989) reported that the biological treatment of AOX at a Finnish hardwood and softwood mill resulted in a 73% reduction of the chlorinated phenolic compounds across the activated sludge plant. In pilot scale work, Rempel *et al.* (1990) reported that in air-activated sludge treatment with SRT values of greater than 17 days, chlorophenolic compound removal efficiencies were usually over 90%.

In view of the wide range in reported results, the Panel was unable to define precise removal efficiencies for chlorophenolic compounds in the revised fibreline mill. Considering that the degree of chlorination should be reduced by high levels of chlorine dioxide substitution and that with 100% chlorine dioxide the chlorovanillins will tend to predominate (Berry, 1990), the Panel believes that it is reasonable to expect 60 to 80% removal of chlorophenolic compounds. This is provided that the SRT value is maintained in the 18 to 25 day range. The expected long term average chlorophenolic compound discharge rates are thus expected to be between 5.5 g/d and 11.1 g/d for hardwood and between 2.5 kg/d and 5.0 kg/d for softwood.

5.5.5 Dioxin and Furan Removal Efficiency

Despite claims by Alberta-Pacific and PAPRICAN (Transcript, p. 578 and p. 77) that the new fibreline will operate in the "dioxin free" zone, the Panel evaluated the expected removal efficiencies of dioxins in activated sludge plants. The Panel recognized that although the mill might not produce dioxins and furans, it might nevertheless serve to transport background quantities of dioxins/furans in wood to one location for discharge (Transcript, p. 221).

Recent findings of the U.S. EPA 104 mill study (Anderson *et al.*, 1990) show that for U.S. kraft mills, 2, 3, 7, 8-TCDD/F were detected in 90/107 samples (TCDD) and in 104/111 samples (TCDF) of effluent. The mean values were 0.076 ng/kg (TCDD) and 0.48 ng/kg (TCDF). Half the values were less than 0.035 ng/kg and 0.1 ng/kg respectively and 17 (TCDD) and 7 (TCDF) samples exhibited values below the detection limits (0.003 to 0.017 ng/kg). Mills using activated sludge treatment released less effluent-based TCDD/F but more sludge-based TCDD/F than aerated stabilization basins. However, no removal efficiencies were reported. The comment was made that the partitioning of TCDD/F between effluent and sludge was highly variable from mill to mill. It was also noted that mills using oxygen delignification and high levels of chlorine dioxide substitution discharged lower TCDD/F levels.

In two U.S. kraft mills, biological effluent treatment resulted in the transfer of more than 90% of the effluent 2, 3, 7, 8-TCDD/F to the sludge (Amendola *et al.*, 1989). The authors noted that chemically assisted final clarification appeared to be an effective control mechanism, but pointed out that improved suspended solids removal in existing facilities may be quickly and easily implemented as an interim control measure. It seems that reducing the effluent total suspended solids discharges to less than 70 mg/L reduces the effluent TCDD/F levels to below the detection limits.

The Panel can draw no conclusions about the removal efficiencies of 2, 3, 7, 8-TCDD/F in the proposed extended aeration activated sludge plant. Should background dioxins and furans associated with the wood be concentrated and transferred to the effluent by the revised fibreline, it is probable that they will be largely removed with the waste sludge. The 2, 3, 7, 8-TCDD/F levels in the effluent should, therefore, be undetectable at present detection limits of 5 - 20 ppq.

5.5.6 Sludge Disposal

The Panel is unaware of information regarding the partitioning of AOX between primary and secondary sludges produced in kraft mill wastewater treatment plants. It has been assumed, therefore, that what is known regarding secondary sludge AOX contents can be applied to primary sludge. This assumption will give conservative estimates of AOX release to the environment from sludges.

Skogman (1989) has shown that 3.5% of the AOX and 2% of the chlorinated phenolic compounds entering a Finnish activated sludge plant leave with the secondary sludge. That plant produces 0.5 kg of sludge for each 1 kg of BOD_5 removed, amounting to 9 tonnes/day of sludge. Totals of 315 kg of AOX and 180 g of chlorinated phenolic compounds are removed each day with the waste sludge. In that mill, the sludges are incinerated in the manner proposed by Alberta-Pacific. In the Aanekoski mill, also in

Finland, the sludge from the activated sludge plant accounts for the removal of 5.9 - 12.5% of the AOX and 2.6 - 10% of the chlorophenolic compounds applied in the influent (Gergov *et al.*, 1988). The Rempel *et al.* (1990) pilot studies report claimed that "the AOX contained in the waste sludge would represent no more than a few percent of the reduction across the full-scale activated sludge plant...."

For the purpose of the following evaluation, the Panel assumed that in the wastewater treatment plant, 10% of the influent AOX and chlorinated phenolic compounds would be transferred to the waste sludge that is to be burned in the hog fuel boiler. This would result in AOX and chlorophenolic compound feed rates to the boiler of up to 3.65 kg/h and 0.014 kg/h respectively.

In a recent emission test of a hog fuel boiler, reported by Environment Canada and the Ministry of Environment of British Columbia (1989), chlorophenols were fed to the boiler at rates up to 7.3 kg/h. At that rate, the destruction and removal efficiency (DRE) for chlorophenol was reported to be 99.9963%. If this performance were to be repeated in the proposed Alberta-Pacific mill, the emissions would be 3.2 g/d for AOX and 12.4 mg/d for chlorinated phenolic compounds; insignificant fractions of the waterborne discharges. During that British Columbia study, the hog fuel boiler was also found to be effective at destroying dioxins and furans. The lowest DRE reported for that study for dioxins and furans was 99.9993%.

5.5.7 Volatilization of AOX

The Panel received a presentation from Mr. M. Bronaugh (Transcript, p. 711) on the subject of volatilization of AOX compounds in biological waste treatment systems. The research of Dr. J. Eisenreich of the University of Minnesota was also referred to in this context (Transcript, p. 724). In his studies on the waste treatment plant of a Finnish mill, Skogman (1989) reported that "stripping of volatiles can be disregarded". It is not clear if measurements were made to support this statement or if it was simply an opinion. In the Aanekoski mill studies, chloroform and chloroacetones levels were measured in the treatment plant influent and effluent. Chloroform was reduced by 63 - 90% and the chloroacetones were reduced by 91 - 100% (Gergov *et al.*, 1988). Again, it is unclear if these were lost through volatilization or biodegradation. The results of Matter-Muller *et al.* (1980), discussed in Leuenberger *et al.* (1985) leave little doubt that volatilization is the dominant removal process for non-biodegradable compounds with an octanol-water partition coefficient log $K_{ow}<5$ and a Henry coefficient $H>10^{-3}$ atm.m^3/mol.

The Panel was unable to gather any information on volatile or purgeable AOX (POX) from mills operating a "chlorine free" bleaching process. The literature does, however contain recent papers by Dallons, *et al.* (1990) and Crawford and Stryker (1988) and a review by Hrutfiord and Negri (1990) on chloroform formation. In all cases chloroform formation is associated with the use of a hypochlorite stage in the bleaching process. Research by Hall *et al.* (1989) indicated POX values for four Canadian bleach plants ranging from 9 g/t to 220 g/t. The POX values in the three softwood bleach plants studied were less than 3% of the AOX. In the hardwood bleach plant the POX value was 12.4% of the AOX. Hynninen (Transcript, p. 576) suggested that the Alberta-Pacific value might be 5%. If the 12.4% and 3% can be assumed to be applicable to the Alberta-Pacific situation (unlikely because of the 100% chlorine dioxide substitution) and the estimated AOX bleach plant discharge rates were 0.45 and 0.7 kg/ADt for hardwood and softwood, the POX values would be 56 g/ADt and 21 g/ADt respectively. If all of the POX were

volatilized in the wastewater treatment plant, the daily average emission rates of POX would be 84 kg/day for hardwood and 26 kg/day for softwood. (Hynninen's number would be 30 kg/day.) It is important to note that the POX would be largely composed of chloroform (Hall *et al.*, 1989).

These emission rates are three orders of magnitude greater than the rates of emission of chlorobenzenes and chlorophenols from a well-run municipal waste incinerator equipped with a two stage electrostatic precipitator (Environment Canada, 1988).

The issue of volatile chlorinated organic emissions was not specifically dealt with by the EIA Review Board which found, among other things, "...the proposed mill acceptable in terms of effects of emissions to the atmosphere" (EIA Review Board, 1990; p. 57). The Panel believes that the revised fibreline mill would not have significantly different volatile emission rates than the original mill and does not dispute the Review Board's finding. However, it would seem prudent for Alberta-Pacific to undertake some experimental research to determine the accuracy of the Panel's estimates of POX emission rates. It may be necessary to consider the need to provide mitigative measures, such as bleach plant effluent air stripping, to reduce the volatile emissions.

5.5.8 Chlorate in Treated Effluents

Dr. D. Schindler raised the issue of chlorate discharges in mill effluents (Schindler, 1990) in the following manner, "According to Scandinavian sources, high substitution of chlorine dioxide for free chlorine causes high production of chlorates." Dr. P. Hynninen estimated that Alberta-Pacific's discharge rate of chlorate could be 2 - 5 kg/ADt of pulp with a 90% reduction rate in the wastewater treatment plant (Transcript, p.582). At the predicted flow rate of 0.7 m^3/s the concentration of chlorate before and after treatment would be 50-124 mg/L and 5 - 12.4 mg/L respectively.

In E.B. Eddy's Espanola mill trials of chlorine dioxide substitution levels of between 10 and 50%, no trend was observed in chlorate concentrations in the influent to the wastewater treatment plant, the values being between 31 and 37 mg/L. The chlorate levels in the effluent were always below detection limits (Munro *et al.*, 1990).

As explained above, the Panel believes that the chlorine dioxide consumption of the revised fibreline mill will be less than that of the original mill. Chlorate discharge was not considered to be an issue by the EIA Review Board and no new evidence has been presented to the Panel to suggest that this should change.

5.6 References

Alberta Environment (1989). "Wastewater Treatment Design Guidelines for Bleached Kraft and CTMP Pulp and Paper Mills", Edmonton, Alberta.

Alberta-Pacific Environmental Impact Assessment Review Board (1990). "The Proposed Alberta-Pacific Pulp Mill: Report of the EIA Review Board". February 28, Edmonton, Alberta.

Alberta-Pacific Forest Industries Inc., Beak Consultants Ltd. and H.A. Simons Ltd. (1990). "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds". Submission No. 46 to The Alberta-Pacific Scientific Review Panel, September 14, Edmonton, Alberta.

Amendola, G.A., Hardy, R.E. and Bodien, D.G. (1989). "Bench-scale study of dioxins and furan (2, 3, 7, 8-TCDD and 2, 3, 7, 8-TCDF) treatability in pulp and paper mill wastewaters". Tappi Journal **72**(12): 189-195.

Anderson, D., Heath, G., Helms, J., Kahn, H.D., Smith, M.D., and Williams, R. (1990). "Findings of US EPA/Paper Industry Cooperative Dioxin Study-The 104 Mill Study". Proceedings of the Dioxin '90 Conference. In the Proceedings of the International Conference on Organohalogen Compounds. Bayreuth, FRG. September 10-14.

Becker, E. and M. Holloran (1990). "Alberta-Pacific Lab Scale Pulping and Bleaching Trial B-1444-1". Submission No. 31 to The Alberta-Pacific Scientific Review Board, September 13, Athabasca, Alberta.

Berry, R. (1990). Overheads for Oral Presentation. Submission No. 26 to The Alberta-Pacific Scientific Review Panel, September 14, Athabasca, Alberta.

Cook, R.C. (1988). "Organochlorine Discharges From A Bleached Kraft Pulp Mill with Oxygen Delignification and Secondary Treatment System". Proceedings of the 1988 Environment Conference, CPPA Technical Section, p. 37. (Recently published in Pulp and Paper Canada **91**(8): T305-310 (1990).

Crawford, R.J. and Stryker, M.N. (1988) "Factors that Affect the Generation of Chloroform in Bleaching". Tappi Journal, **71**(11):151-159.

Dallons, V.J., Hoy, D.R., Messmer, R.A. and Crawford, R.J. (1990). "Chloroform Bleaching and Release from Pulp Bleaching". Tappi Journal, **73**(6): 91-95.

Earl, P.R. and Reeve, D.W. (1989). "Chlorinated Organic Matter in Bleached Chemical Pulp Production, Part III: The Effect of Chlorination Stage Variables on Chlorinated Organic Matter in the Effluent". Tappi Environmental Conference, Orlando, Florida, April 17-19.

Environment Canada (1988). "Summary Report of the National Incinerator Testing and Evaluation Program: Environmental Characterization of Mass Burning Incinerator Technology at Quebec City. Report EPS 3/UP/5, June 1988.

Environment Canada and Ministry of Environment, British Columbia (1989). Summary Report entitled, "A Test Burn of Chlorophenol Contaminated Woodwastes at Northwood Pulp Mill Prince George, B.C."

Fraser, J.L. and Reeve, D.W. (1990). "Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part V - An Interlaboratory Comparison of Techniques and Test Results for AOX Analysis in Effluents" presented at the 76th Annual Meeting of the Technical Section of the Canadian Pulp and Paper Association, January, 1990.

Gergov, M., Priha, M., Talka, E., Valtila, O., Kangas, A. and Kukkonen K. (1988). "Chlorinated Organic Compounds in Effluent Treatment at Kraft Mills". Tappi Journal,**71**(12): 175-184.

Germgard, U. and Larsson, S. (1983). "Oxygen Bleaching in the Modern Softwood Kraft Mill". Paperi ja Puu, **65**(4): 287.

Germgard, U. (1982). "Kinetics of Prebleaching Softwood Kraft Pulp with Chlorine Dioxide and Small Fractions of Chlorine". Paperi ja Puu, **1982**(2): 76-82.

Hall, E.R., Fraser, J., Garden, S. and Cornacchio, L.A., (1989). "Organo-chlorine discharges in Wastewaters from Kraft Mill Bleach Plants". Pulp and Paper Canada, **90**(11): T421-T425.

Heimburger, S.A., Blevins, D.S., Bostwick, J.H. and Donnini, G.P. (1988). "Kraft Mill bleach plant effluents: recent developments aimed at decreasing their environmental impact, part 2. Tappi Journal, **71**(11): 69-78.

Hong, C.C. and Rapson, W.H. (1968). "Kinetics of Disproportionation of Chlorous Acid", Can. J. Chem., **46**:2053-60 (1968).

Hrutfiord, B.F., and Negri, A.R. (1990). "Chemistry of Chloroform formation inpulp bleaching: a review". Tappi Journal, **76**(6): 219-225.

Kolar, J.J., Lindgren, B.O. and Petterson, B. (1983). "Chemical Reactions in Chlorine Dioxide Stages of Pulp Bleaching". Wood Sci. Technol., **17**:117-128.

Leuenberger, C., Giger, W., Coney, R., Graydon, J.W. and Molnar Knbica, E. (1985). "Persistent Chemicals in Pulp Mill Effluents. Water Res., **19**(7): 885-894.

Malter-Müller C., Gujer, W., Giger, W. and Stumm, W. (1980). "Non-biological elimination mechanisms in a biological sewage treatment plant. Prog. Wat. Technol., **12**:299-314.

McCubbin, N. (1990). "Comments on Alberta Pacific Forest Industries Inc. Response to Concerns Regarding Chlorinated Organics. Submission #21 to the Alberta-Pacific Scientific Review Panel, August 30, Edmonton, Alberta.

Munro, F.C., Chandrasekaran, S., Cook, C.R., and Pryke, D.C. (1990). "Impact of High Chlorine Dioxide Substitution For Chlorine on the Oxygen Delignified Pulp at Espanola". 1990 Tappi Environmental Conference Preprints, Vol. 2, p. 491-502.

Rappe, C., Glas, B., deWit, C. and Melin, A. (1989). "Levels of PCDD and PCDFs in Swedish Paper Industry Products". Poster Presentation, Dioxin 89 Conference, Toronto, September 1989.

Reeve, D.W. (1990a). Overheads for Oral Presentation. Submission No. 25 to The Alberta-Pacific Scientific Review Panel, September 12, Athabasca, Alberta.

Reeve, D.W. (1990b). Unpublished results from the Pulp and Paper Centre, Univeristy of Toronto.

Reid, D.W., G.G. Billmark and C.J. Sutton (1990). "Peroxide Bleaching Reduces Dioxin Formation in a Generator Limited Mill". Presented at Western Section Meeting, Technical Section, CPPA, May, Jasper, Alberta.

Rempel, W., Turk, O. and Sikes, J.E.G. (1990) "Side-by-side Activated Sludge Pilot Plant Investigations Focussing on Organochlorines". 1990 CPPA Jasper Conference.

Schindler, D.W. (1990). "Possible Effects of the Proposed Alberta Pacific Mill on the Athabasca River — Comments on Proposed Mitigation Measures". Submission No. 5 to the Alberta-Pacific Scientific Review Panel, August 22, Edmonton, Alberta.

Skogman, R. (1989). "Biological Treatment of Chlorinated Organic Matter in Pulp Mill Effluents". Third Colloquium on Pulp and Paper Mill Effluents, University of Toronto, Pulp and Paper Centre.

Stanley Associates Engineering Ltd. (1989). "Alberta-Pacific Forest Industries Inc. Pulp Mill Effluent Treatment Plant 3605-d, AREA 17: Pre-Design Report". Job. No. 71-194-01-09, Alberta-Pacific Forest Industries Inc., November, Edmonton, Alberta.

Suess, H.U., Eul, W.L., Nimmesfroh, N. and Meier, JJ. (1990). "Environmental Aspects of Short Sequence Bleaching". Tappi Environmental Conference, Seattle, p. 503-513.

Sullivans, T.W. (1980). "Organic Chemistry". 2nd Edition, Wiley, N.Y.

Teder, A. and Tormund, D. (1977). "Kinetics of Chlorine Dioxide Bleaching". Transactions of the Technical Section, CPPA, **3**(2): 41-46 (June, 1977).

Voss, R.H., Wearing, J.T., and Wong, A. Pulp and Paper Canada **82**(2): T65 (1981).

Voss, R.H. Luthe, C.E., Fleming, B.I., Berry, R.M. and Allen, L.H. (1988). "Some New Insights into the Origins of Dioxins formed during Chemical Pulp Bleaching". Pulp and Paper Canada, **89**(12), 157-161. (1988).

Wartiovaara, I. (1982). "A theoretical model for the reaction mechanism of chlorine dioxide bleaching", Paperi ja Puu-Papper och Trä 1982 (11): 680-683.

Section 6—Accidental Discharges

The potential for accidental discharges of pollutants was briefly discussed in the Review Board's report. This discussion occurred in the context of a general analysis of Emergency Response (EIA Board, 1990). The Review Board concluded that the safety mechanisms proposed for the mill site (including spill control) were reasonable and that emergencies should not be common events. It went on to recommend a number of steps to ensure that adequate emergency response planning would be in place prior to plant start up.

One submittor to the Panel (Arrison, 1990) recommended a complete and comprehensive accident risk assessment of the Alberta-Pacific proposed mill with particular regard for releases of chlorinated organics damaging to the Athabasca River. Based on a preliminary HAZOP assessment, he predicted that a major explosion would occur at this plant once every 19 years and that accidental effluent discharges would occur once every 34.3 days. He acknowledged that adequately detailed information was not available to permit a comprehensive analysis of the proposed plant. In addition, the short deadlines did not allow for complete analysis of the information which was available.

Countering these predictions were comments from a number of other technical experts that the nearly forty years of operation of chlorine dioxide bleaching towers indicated little or no history of serious accidents.

Following the Workshop, the Panel pursued this matter further. It contacted the American Paper Institute, the Canada Center for Occupational Health and Safety and the Canadian Pulp and Paper Association. There appears to be no record of catastrophic chlorine dioxide explosions in pulp mill bleach plants. All of the organizations contacted reported that they were generally unaware of occurrences of failures of the magnitude suggested.

Based on the knowledge and experience of the Panel members and advisors, the Panel believes that processes for manufacture of chlorine dioxide are carefully and deliberately designed to be safe. This is embodied in the physical design, the operating conditions and procedures, the computer-controlled interlocks and the upset/fail-safe strategies and equipment used in chlorine dioxide generators. For the vacuum-type generators such as that selected by Alberta-Pacific, there are some 500 operating years of experience without any explosion which ruptured a vessel.

In pulp bleaching, heated pulp and chlorine dioxide solution are separately pumped to a mixer and then let into a large retention tower. In the worst case, chlorine dioxide solution, accidentally pumped into a chlorine dioxide tower without pulp, could undergo a temperature increase. The accumulation of chlorine dioxide vapour in the tower could lead to a decomposition and a pressure increase of perhaps 300-400 kPa (kilopascals). Chlorine dioxide towers are, however, designed with vents which will relieve excess pressure (Torregrossa *et al.*, 1976).

The bleaching of pulp with chlorine dioxide solution has been widely practised since about 1950. There are many thousands of operating years experience with chlorine dioxide bleaching towers. Catastrophic chlorine dioxide explosions in such towers appear to be virtually unknown.

With respect to the question of accidental discharges, the Panel notes that spike discharges are most likely to originate from upsets involving highly concentrated solutions held in inventory. Black liquor, for instance, is produced and stored at very high BOD_5 concentrations. However, there are no such concentrated or stored solutions of organochlorine compounds in a bleached kraft pulp mill. The Panel can see no reason for "accidental" releases of organochlorine compounds to occur.

The Panel agrees that safety measure and emergency response planning should be an integral part of the design and operational planning for the proposed mill. It also concludes, that there does not appear to be any need to be unduly concerned with the potential for explosions or accidental release of chlorinated organic compounds.

At the Workshop, the Panel asked for and received a further commitment from Alberta-Pacific that it is committed to safe operation and the development of comprehensive emergency response plans that have been adequately reviewed with the potentially affected public (Fenner, Transcript, p. 621 - 622). The Panel believes that the appropriate regulatory authorities, such as Alberta Environment, should monitor this situation and ensure that these commitments are fulfilled.

6.1 References

Alberta-Pacific Environmental Impact Assessment Review Board (1990). "The Proposed Alberta-Pacific Pulp Mill: Report of the EIA Review Board". February 28, Edmonton, Alberta.

Arrison, N.L. (1990). "Probable Accidental Discharges of Chlorinated Organic Compounds from the Alberta-Pacific Forest Industries Inc. Pulp Mill Into the Athabasca River. A Preliminary HAZOP Review of the Mill Safety Design". Submission No. 12 to the Alberta-Pacific Scientific Review Panel, August 22, Edmonton, Alberta.

Torregrossa, L., R. Justice, Schleinkofer and K. Vogel (1970). "Decomposition of Gaseous Chlorine Dioxide". Tappi Journal, **59**(11): 92-93.

Section 7—Conclusions

7.1 Technical Feasibility of Revised Pulping and Bleaching Processes

- The technology proposed for the revised Alberta-Pacific fibreline is feasible.
- The revised fibreline incorporates a sufficient degree of robustness to consistently achieve the chlorinated organic matter discharge rates forecasted by the Panel.
- Additional mitigating options are available to allow retrofitting of the Alberta-Pacific mill to further reduce the organochlorine discharge, if required.
- A continous flow pilot demonstration of the proposed fibreline technology is neither desirable nor feasible.

7.2 Expected Effluent Characteristics

The Panel's estimates of the daily discharge rates of chlorinated organic matter from the revised Alberta-Pacific mill are shown for hardwood in Figure 7.2.1 and for softwood in Figure 7.2.2.

- The wastewater treatment plant design is still evolving; however the basic approach appears to be satisfactory.
- The proposed fibreline and wastewater treatment technology is capable of limiting waterborne discharges of AOX to 0.32 kg/ADt for hardwood pulp, and 0.49 kg/ADt for softwood pulps, over the long term. The long term hardwood plus softwood weighted average discharge would be less than 0.35 kg AOX/ADt.
- The proposed fibreline and wastewater treatment technology is capable of limiting waterborne discharges of chlorophenolic compounds to a maximum of 4.0 g/ADt. The long term hardwood plus softwood weighted average discharge would be less than 840 mg/ADt.
- The bleach plant technology would not produce detectable increases of 2, 3, 7, 8-tetrachlorodibenzo-para-dioxin or 2, 3, 7, 8-tetrachlorodibenzofuran above background levels.
- The airborne emission of volatile organic material during secondary treatment would be less than 12% of the AOX produced in the bleach plant.
- The incineration of sludge will not result in significant emissions of AOX or chlorinated phenolic compounds to the environment.
- The mill can be designed with adequate safety features to prevent accidental discharges of chlorinated organic matter.

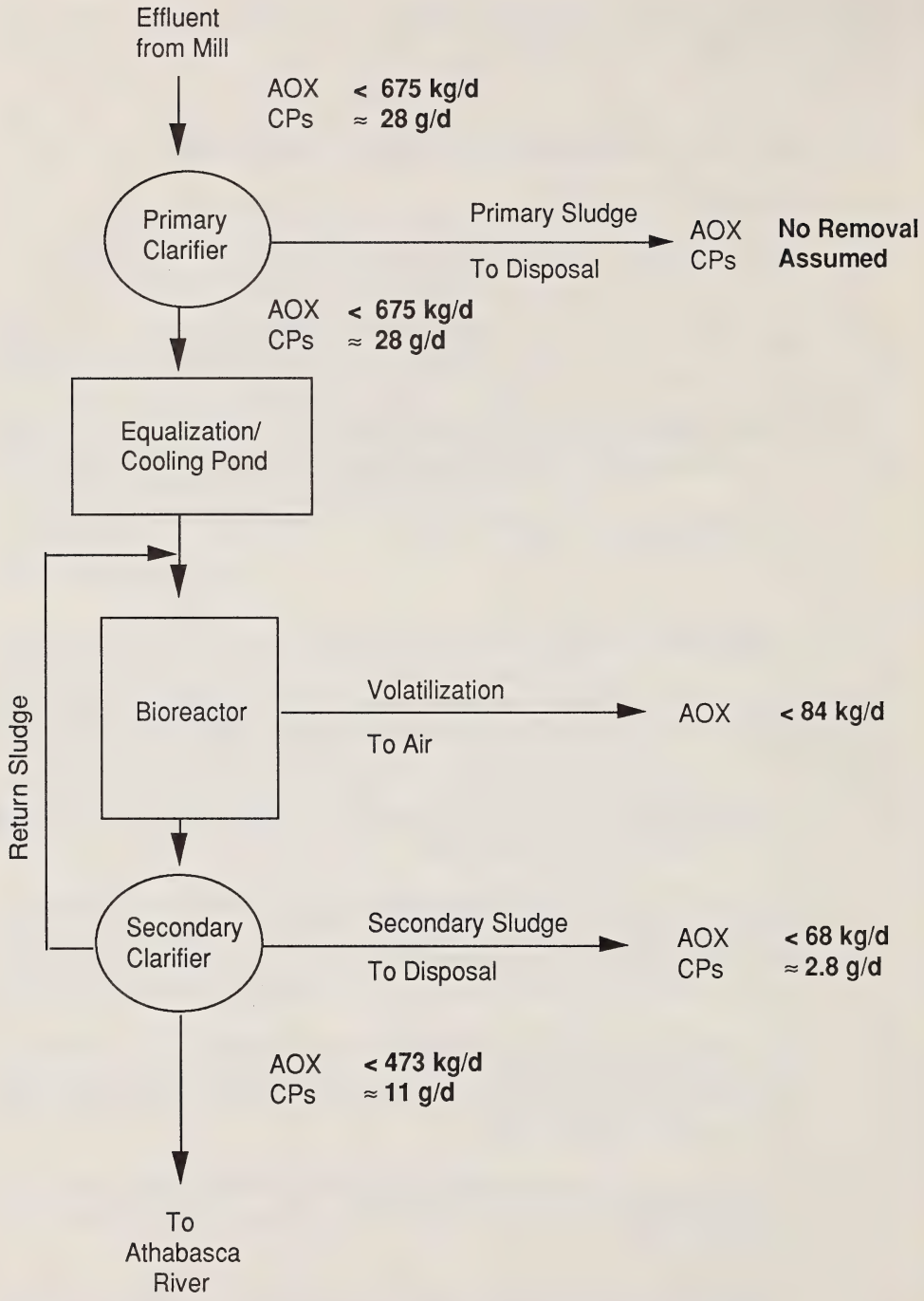


Figure 7.2.1 Panel Estimates of Maximum Long Term Average Discharges of AOX and Chlorinated Phenolics (CPs) During Hardwood Pulping.

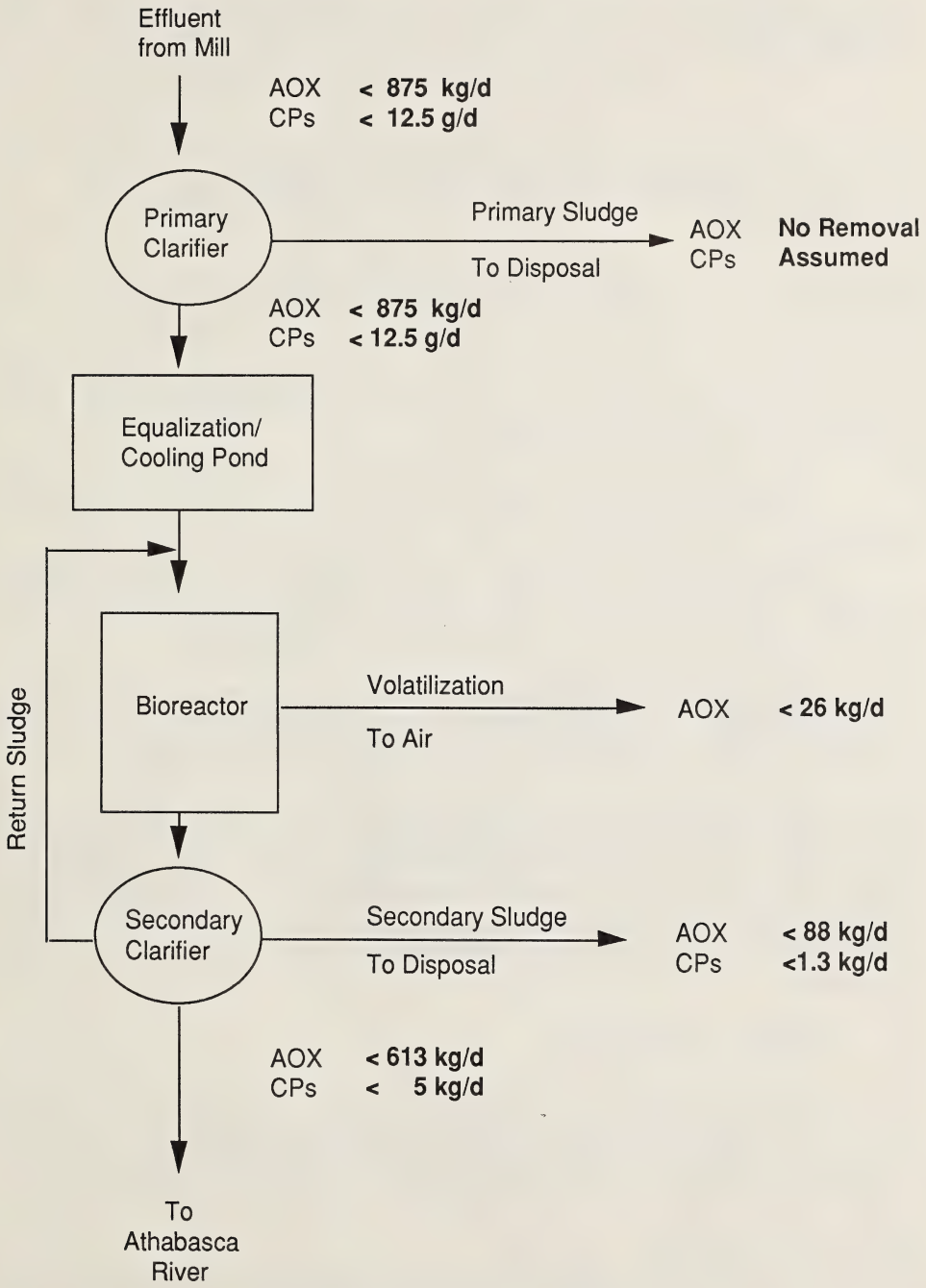


Figure 7.2.2 Panel Estimates of Maximum Long Term Average Discharges of AOX and Chlorinated Phenolics (CPs) During Softwood Pulping.

Appendix 1

The Department of the Environment Act

Ministerial Order No. 9/90

WHEREAS the Minister of Environment (the "Minister") may establish a panel to act in an advisory capacity in connection with any of the policies, programs, services, or other matters under his administration.

AND WHEREAS Alberta-Pacific Forest Industries Inc. has proposed a bleached kraft pulp mill in the County of Athabasca.

AND WHEREAS Alberta-Pacific Forest Industries Inc. has proposed further mitigation measures to respond to the Alberta-Pacific EIA Review Board concerns about the discharge of chlorinated organics into the Athabasca River.

AND WHEREAS it is necessary and desirable to conduct a scientific review of the improvements to the wood-pulping process as they relate to the mitigation of the chlorinated organics as proposed by Alberta-Pacific Forest Industries Inc.

THEREFORE I, RALPH P. KLEIN, Minister of the Environment, pursuant to Section 6 of the Department of the Environment Act, hereby establish a panel to be know as "the Alberta-Pacific Scientific Review Panel" (the "Review Panel") to advise and make recommendations upon the improvements proposed by Alberta-Pacific Forest Industries Inc. to the wood-pulping process as they relate to the mitigation of the discharge of chlorinated organics into the Athabasca River upon the following terms and conditions:

A. TERMS OF REFERENCE

The Terms of Reference of the Review Panel shall be to inquire into and advise the Minister of the Environment on the improvements proposed by Alberta-Pacific Forest Industries Inc. to the wood-pulping and bleaching process as they relate to the mitigation of the discharge of chlorinated organics into the Athabasca River.

B. PROCEDURES

1. The Review Panel shall invite and consider timely written submissions from the public that the Review Panel considers relevent (sic) to the proposed improvements to the wood-pulping process as they relate to the mitigation of the discharge of chlorinated organics into the Athabasca River, receipt of submissions from the public to be not later than Wednesday, August 22, 1990.

2. The Review Panel shall review the written submissions and determine those public submissions which will be invited to augment their submission by making expert oral presentations to the Review Panel and advise those invited accordingly during the time period August 22 to August 31, 1990.

3. The Review Panel shall receive oral presentations and provide for cross-examination of further scientific evidence from those invited to augment their submissions under (2) above, and hear such presentations on September 12, 13, and 14, 1990 in Athabasca.

4. The Review Panel shall prepare its report on the basis of all submissions, the report to be completed and delivered to the Minister of the Environment when ready but in any event no later than October 1, 1990.

3. MEMBERSHIPS

The Review Panel shall consist of the members set out on the attached Schedule "A".

DATED at the City of Edmonton, in the Province of Alberta, this 12 day of July, 1990.

RALPH P. KLEIN
MINISTER OF THE ENVIRONMENT

Schedule "A"

Membership

of

the Alberta-Pacific Scientific Review Panel

NAME

1. Mr. Ed Brushett, (Chairman) Alberta Energy Resources Conservation Board, Calgary, Alberta

2. Dr. Malcolm Wilson, Alberta Environmetnal (sic) Centre, Vegreville, Alberta

3. Dr. Eric Hall, Waste Water (sic) Technology Centre, Burlington, Ontario

Appendix 2

Scientific and Technical Discussions Before the Review Panel September 12-14, 1990 Nancy Appleby Theatre, Athabasca

Wednesday, September 12, 1990

am
- Opening Remarks and Introductions—Panel Chairman, E.R. Brushett
- Technical Introduction—Dr. D. Reeve, Panel Advisor
- Presentation—Dr. R. Berry, Pulp and Paper Research Institute of Canada
- Presentation—Dr. K. Sarkanen, University of Washington

pm
- General Discussion
- Presentation—Dr. W. Harris and Dr. M.A. Armour, University of Alberta
- General Discussion

evening
- Discussion of Bleaching Trial Data

Thursday, September 13, 1990

am
- Continuation of Bleaching Trial Data Discussion
- Presentation—Dr. J. Plambeck, University of Alberta
- General Discussion
- Presentation—Mitch Bronaugh, Edmonton
- General Discussion

pm
- Presentation—Ed Barnes, Burnaby, British Columbia
- Report—Ed Barnes, Burnaby, British Columbia
- General Discussion
- Report—Dr. D. Reeve, Panel Advisor
- Presentation—Dr. N. Arrison, Edmonton
- General Discussion

Friday, September 14, 1990

am
- Questions to Alberta-Pacific
  - from Panel members
  - from Panel staff

pm
- Questions to Alberta-Pacific
  - from Panel members
  - from presenters
- General Discussion

Appendix 3

Alberta-Pacific Scientific Review Panel Submissions

Date	From	Submission #
August 14/90	Michael Gismondi Chair, Technical Committee Friends of the Athabasca (FOTA)	1
August 20/90	W.A. Fuller, Ph.D. Professor Emeritus, University of Alberta	2
August 21/90	E.C.M. (Betty) Collicot, Mayor City of Fort McMurray	3
August 21/90	G. F. Paschen, Director Canadians for Responsible Northern Development	4
August 22/90	D. W. Schindler, D. Phil., F.R.S.C. Killam Memorial Professor of Ecology Departments of Botany and Zoology University of Alberta	5
August 21/90	James O. Darwish	6
August 22/90	E. C. Hanson Concerned Voter, Taxpayer and Citizen	7
August 22/90	M.A. Armour, Ph.D. and W.E. Harris, Ph.D. Department of Chemistry University of Alberta	8
August 22/90	James A. Plambeck, Ph.D. Associate Professor Department of Chemistry University of Alberta On behalf of: Canadians for Responsible Northern Development	9
August 23/90	Revised P.H. Sutherland, Director General Central & Arctic Region Department of Fisheries and Oceans	10

Date	From	Submission #
August 22/90	Mitch Bronaugh	11
August 22/90	N.L. Arrison, Ph.D., P.Eng. WHMIS Inc. On behalf of: Brian Toole	12
August 22/90	Randy Lawrence	13
August 22/90	Andy Boyd, President Sherwood Park Fish & Game Association	14
August 22/90	John McInnis, M.L.A. Edmonton Jasper Place New Democrat Spokesperson Environment and Forestry	15
August 23/90	Dr. Peter Wrist and Dr. Richard Berry Pulp and Paper Research Institute of Canada, Pointe Claire, Quebec	16
August 10/90	David J. Parker, P.Eng. Northern Alberta Institute of Technology	17
August 24/90	Brian Killeen, B.Sc. Marine Biology and Renate Kroesa, M.Sc. Chemistry Greenpeace Vancouver	18
August 22/90	L. Hrubizna, Edmonton	19
August 22/90	Mary Richardson, Athabasca	20
August 30/90	Neil McCubbin, B.Sc. N. McCubbin Consultants Inc.	21
August 30/90	E.T. Barnes, P.Eng. E.T. Barnes and Associates Inc.	22

Alberta-Pacific Scientific Review Panel

Additional Submissions and supplementary material received and/or registered after August 30, 1990

Date	From	Submission #
Sept. 5/90	D. W. Schindler, D. Phil., F.R.S.C. Killam Memorial Professor of Ecology Departments of Botany and Zoology University of Alberta	5.1
Sept. 7/90 Sept. 10/90	Mitch Bronaugh	11.1 11.2
Sept. 11/90	Steven J. Eisenreich Professor of Environmental Chemistry Department of Civil and Mineral Engineering University of Minnesota	23
Sep. 12/90	Overheads—E.R. Brushett Opening Remarks	24
Sept. 12/90	Overheads Introductory Presentation Dr. Doug Reeve	25
Sept. 12/90	Overheads Dr. Richard Berry PAPRICAN	26
Sept. 12/90	Dr. Kyosti V. Sarkanen Professor of Wood Chemistry University of Washington Submission & Overheads	27
Sept.12/90	Michael Gismondi Friends of the Athabasca "COMMENTS ON N. MCCUBBIN'S REVIEW OF ALPAC'S MITIGATIVE PROPOSAL	

Date	From	Submission #
Sept. 12/90	Michael Gismondi Friends of the Athabasca "Critique of Armour & Harris Submission" by Alder Hill Research Group—Oregon	29
Sept. 12/90	Peter Opryshko Prosperity Environmental Association "A Review of the Site Selection Issue"	30
Sept. 13/90	Overheads Dr. Becker and Mr. Holloran Al-Pac	31
Sept. 13/90	Overheads Dr. Plambeck Representing Canadians for Responsible Northern Development	32
Sept. 13/90	Mitch Bronaugh "Critique of ALPAC Claims"	33
Sept. 13/90	Ed Barnes Report on Longview Mill	34
Sept. 13/90	Dr. Lars Lindstrom Chart on Softwood Kraft Pulp (Pertains to E. Barnes presentation)	34.1
Sep. 13/90	Doug Reeve Reports on Iggesund and Korsnäs Mills	35
Sept. 13/90	Mary Richardson	36
Sept. 13/90	Dr. Cornwell's (Al-Pac) Overheads used in questioning Dr. Arrison	37
Sept. 13/90	Dr. Peter Holt	38
Sept. 14/90	Overhead used by Dr. Hynninen (Al-Pac)	39
Sept. 14/90	Overhead used by Mr. Prough (Al-Pac)	40

Date	From	Submission #
Sept. 14/90	Mr. Prough (Al-Pac) Two articles "A mathematical model for two-phase flow in a continuous digester" and "A Review of the Basis for and the Current Status of Modified Continuous Cooking"	41
Sept. 14/90	Overhead used by Mr. Prough (Al-Pac) Kappa Averages—Howe Sound Pulp Co., Ltd.	42
Sept. 14/90	Dr. Arrison Article entitled "Days of Living Dangerously"	43
Sept. 14/90	Dr. Plambeck Overhead	44
Sept. 14/90	Peter Opryshko "A Chronology of Events Concerning the Residents of Prosperity as Related to Alberta Pacific Pulp Mill Proposal"	45
Sept. 14/90	Al-Pac "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds"	46
Sept. 14/90	Al-Pac Errata to "Mitigative Response to Concerns Regarding Chlorinated Organic Compounds"	46.1
Sept. 17/90	W.A. Fuller, Ph.D. Friends of the Athabasca Environmental Assoc. "Critique of the Jaakko Pöyry Report"	47
Sept. 17/90	Laurie McIntyre and Leigh Noton Alberta Environment "Chlorates: A Literature Review of Aspects Relevant to the Aquatic Enviornment	48
Sept. 20/90	Dr. Armour and Dr. Harris University of Alberta Overheads	49
Sept. 20/90	Dr. James A. Plambeck Additional Information	50

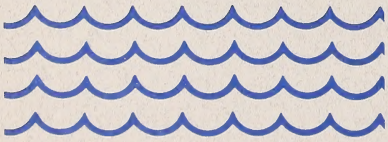
Date	From	Submission #
Sept. 21/90	Mr. Mitch Bronaugh Additional Information	51
Sept. 21/90	Richard Berry PAPRICAN Response to question at Workshop	52
Sept. 24/90	Michael Gismondi Chair, Technical Committee Friends of the Athabasca (FOTA) "Follow Up Issues"	53
Sept. 24/90	Elizabeth Paschen	54
Sept. 24/90	Al-Pac QA/QA program for Resin/Fatty Acids and chlorinated phenolics	55

Appendix 4

The Panel Members' Biographies

Ed Brushett, Chairman, B.Sc. Chemical Engineering 1954, University of Alberta. Brushett is also Special Advisor Environmental Affairs with the Energy Resources Conservation Board. He is a Native Albertan and lives in Calgary.

Malcolm A. Wilson, Ph.D. Organic Chemistry 1969, University of London (U.K.) Director, Environmental Technology Division, Alberta Environmental Centre, in Vegreville, where he also lives. Dr. Wilson is also Vice-Chairman of the Pacific Basin Consortium for Hazardous Waste Research.

Eric R. Hall is a Senior Process Development Engineer at Environment Canada's Wastewater Technology Centre in Burlington, Ontario, where he directs federal research programs on pulp and paper effluent treatment. Dr. Hall is also an Associate Professor in the Environmental Engineering Systems Group at McMaster University. He lives in Hamilton, Ontario.

N.L.C. - B.N.C.
3 3286 10332517 7